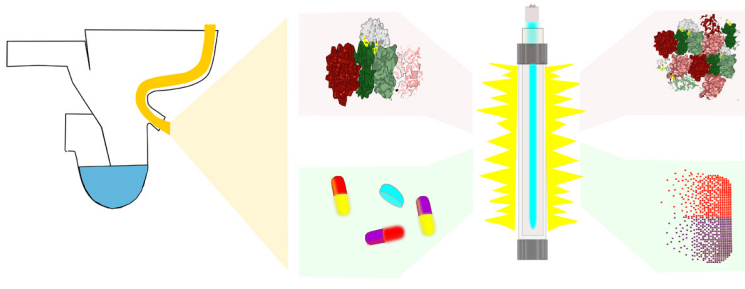
UV-based advanced oxidation process for nutrient stabilisation and organic micropollutant degradation in source-separated human urine

Natnael Demissie



Licentiate Thesis
Swedish University of Agricultural Sciences
Uppsala

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SWEDISH UNIVERSITY
OF AGRICULTURAL
SCIENCES

LICENTIATE THESIS

Uppsala 2024

Cover: UV treatment for enzyme inactivation and pharmaceutical degradation in source separated human urine
Cover illustration by Natnael Demissie

Licentiate thesis / Report 125
ISSN 1654-9406
ISBN (print version) 978-91-8046-897-8
ISBN (electronic version) 978-91-8046-669-1
https://doi.org/10.54612/a.c9s3mcdqlc

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Print: SLU Grafisk service, Uppsala 2023

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Abstract

Urine dehydration is one of the technological approach to recover nutrients in concentrated form from source separated urine. When drying fresh urine, nitrogen loss occurs due to hydrolysis of urea into ammonia unless methods to inactivate urease enzyme are employed. In addition, concerns arise when using urine-derived fertiliser due to the potential presence of organic micropollutants (pharmaceuticals). This thesis evaluated ultraviolet (UV) treatment as an alternative chemical-free nutrient stabilisation (urease inactivation) and organic micropollutant (OMP) degradation technology. Urease inactivation and OMP degradation in water and in urine (synthetic urine, real urine from human subjects) were studied in a photoreactor equipped with a low-pressure mercury UV lamp emitting light predominantly at 185 and 254 nm. Exposure of real urine to 80 min of UV irradiation resulted in more than 90% degradation of 18 out of 75 OMPs and 1-90% degradation of the remaining OMPs. Enzymatic activity fell below the detection limit for real urine exposed to 71 min of UV irradiation. However, electrical energy demand for reducing enzymatic activity below the detection limit in real fresh urine was 52-fold higher than for inactivation in synthetic fresh urine (without urea), while electrical energy demand was more than 10-fold higher for 90% OMP degradation in real fresh urine than in water. The inactivation and OMP degradation observed were probably due to direct photolysis and photo-oxidation. Presence of organic substances in real urine was the likely reason for less efficient inactivation of urease and OMP degradation, as such substances can competitively absorb incoming UV light and scavenge the free radicals formed during UV treatment. Although 20% urea was lost after UV treatment, there was no decrease in total nitrogen. In summary, UV treatment can stabilise urea-N and degrade OMPs in fresh urine and has potential for integration into urine diversion sanitation systems.

Keywords: Circular sanitation, wastewater treatment, urine diversion, nutrient recycling, UV treatment, urease, enzyme inactivation, pharmaceuticals.

UV-baserad avancerad oxidationsprocess för stabilisering av urea-N och nedbrytning av organisk mikroförorening från källseparerad mänsklig urin

Sammanfattning

Urinutorkning är en tekniska metoderna för återvinning av koncentrerade näringsämnen från källsorterad urin. Vid torkning av färsk urin kan förluster av kväve uppkomma beroende av hydrolys av urea som omvandlas till bland annat ammoniak, om inte ureasenzym inaktiveras. Även om näringsinnehållet i urinen prioriteras i ett uthålligt samhälle, finns det oro kring innehållet av organiska mikroföroreningar (läkemedel) i urinen. Denna avhandling utvärderar en alternativ kemikaliefri ureasinaktivering och teknik för nedbrytning av organiska mikroföroreningar (läkemedel). Ureasinaktivering och nedbrytning av organiska mikroföroreningar (OMP), i vatten och i urin (syntetisk urin utan urea och färsk humanurin), studerades i en fotoreaktor utrustad med en lågtrycks UV-lampa som emitterade ljus övervägande vid 185 och 254 nm. Exponering av verklig urin för 80 min UV-bestrålning resulterade i nedbrytning av 18 av 75 OMP:er med mer än 90 % medan resten av OMP:er försämrades mellan 1-90 %. Enzymatisk aktivitet var under detektionsgränsen för verklig urin exponerad för 71 minuters UV-bestrålning. Emellertid var behovet av elektrisk energi för att minska enzymaktiviteten under detektionsgränsen i verklig färsk urin 52 gånger högre än för inaktivering i syntetisk färsk urin (utan urea), medan behovet av elektrisk energi var mer än 10 gånger högre för 90 % OMP-nedbrytning i riktigt färsk urin än i vatten. Inaktivering av ureas och OMP-nedbrytning inträffade sannolikt på grund av direkt fotolys och av fotooxidation. Förekomsten av organiska ämnen i urin var den troliga orsaken till lägre inaktivering av ureas och lägre OMP-nedbrytning eftersom de på ett konkurrerar om att absorbera inkommande UV-ljus och tar upp de fria radikaler som bildas under UV-behandling. Även om 20 % urea bröts ned under UV-behandling, minskade inte mängden totalkväve. Sammanfattningsvis kan UV-behandling stabilisera ureakväve och bryta ned OMPs i färsk urin, vilket visar en potential för integration av UV-behandling i urinledningssystemet.

Keywords: Cirkulär sanitet, avloppsrening, urinavledning, näringsåtervinning, UV-behandling, ureas, enzyminaktivering, läkemedel.

Contents

List of publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

I. Demissie, N., Simha, P., Vasiljev, A. and Vinnerås, B. (2023). Photoinactivation of jack bean (*Canavalia ensiformis*) urease in fresh human urine using dichromatic low-pressure UV lamp. (Manuscript under review)

II. Demissie, N., Simha, P., Lai, F.Y., Ahrens, L., Mussabek, D., Desta, A. and Vinnerås, B. (2023) Degradation of 75 organic micropollutants in fresh human urine and water by UV advanced oxidation process. *Water Research* 120221.

The contribution of Natnael Demissie to Papers I and II was as follows:

I. Designed the experiment together with BV and PS, performed the laboratory work together with PS and AV, wrote the paper together with PS and BV.

II. Designed the experiment together with BV, LA and FYL, conducted the experiment, analysed the results together with FYL, wrote the paper together with PS and FYL.

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1.Introduction

Sanitation was a challenge in the early Mesopotamian empire and is still a problem today, especially in developing countries (Lofrano *et al.*, 2010). Although sanitation has advanced from pit hole burying to properly monitored sewer systems and improved hygiene conditions, there are still challenges in providing sanitation access to all (Mara *et al.*, 2018). One of the United Nations Millennium Development Goals (MDGs) established to address the sanitation challenge was "halving the proportion of people without sustainable access to safe drinking water and basic sanitation", a target to be achieved by 2015 (UN, 2015). However, by that deadline only 95 out of 172 countries had met the sanitation target (UN, 2015). In 2015, the sanitation agenda was included in the Sustainable Development Goals (SDGs), where an ambitious target set was to provide adequate sanitation and hygiene access to all by 2030 (UN, 2023). Other targets to be achieved by 2030 are ending open defecation, improving wastewater treatment and safe reuse of nutrients in excreta.

A recent assessment by the joint monitoring programme (JMP) of progress towards the SDGs found that between 2015 and 2020 there was only a 7% increase, from 49% to 57%, in the population with access to safely managed sanitation (UN, 2023). Some countries (South Korea, Switzerland, Austria) had achieved SDG-6 sub-targets such as provision of sanitation service to all and safe management of wastewater, but some developing countries (Ethiopia, Togo, Chad) were only less than 15% of the way towards achieving the targets, requiring quadrupling of efforts to meet the overall target by 2030 (Ritchie *et al.*, 2018; UN, 2022).

The JMP report released by UN (2023) also mentioned that progress towards the SDG-6 sub-target on water quality is frequently failing due to phosphorus and nitrogen release from agriculture and untreated wastewater. While wastewater treatment plants with secondary treatment processes are designed to remove organic matter, these processes are inefficient in removing nitrogen (N), which poses a eutrophication threat in receiving water streams (Li *et al.*, 2017). Urine represents 80% N and 50% P load of domestic wastewater, but its volumetric contribution is only 1% (Vinnerås *et al.*, 2006).

Source separation and recovery of nutrients from urine and their subsequent use in agriculture is among circular economy approaches that can help realise SDG-6 (Larsen *et al.*, 2021a; Mcconville *et al.*, 2020). Following large-scale separation of urine in urban setting and use on agricultural land or in commercial applications the urine needs to be concentrated, as otherwise nutrient reuse would be uneconomical due to logistical challenges (Dutta *et al.*, 2016; Senecal-Smith, 2020). Different nutrient-concentrating technologies have been developed (for a thorough review, see Larsen *et al.* (2021a). One of these is urine drying, a technology that concentrates urine and recovers all macronutrients (Urea-N, P and potassium (K)) and micronutrients (Senecal *et al.*, 2017; Vasiljev *et al.*, 2021). However, when concentrating the nutrients by drying, urine must be stabilised to minimize N loss due to hydrolysis of urea-N by urease enzyme (Senecal *et al.*, 2017). Otherwise, hydrolysis of urea in urine leads to loss of nitrogen and phosphorus in urine-diverting toilets or urine storage tanks in the form of scales and free ammonia gas (Geinzer, 2017; Udert *et al.*, 2003b).

Urease, a ubiquitous enzyme in nature and in sanitation systems, is responsible for hydrolysis of urea in source-separated urine into ammonia and bicarbonate (Udert *et al.*, 2003a). The ammonia formed during hydrolysis will be lost when the urine is subjected to drying, leading to very low nitrogen recovery. Acidification (Boncz *et al.*, 2016), alkalisation (Simha *et al.*, 2020b) or treating urine with electrochemical oxidation (De Paepe *et al.*, 2020) are among the technologies reported to halt the enzymatic action of urease. However, use of chemicals requires active monitoring, and therefore chemical-free stabilisation technology is preferable. When the nutrients in urine have been stabilised and concentrated, with chemicals or

by other methods, concerns still arise regarding presence of organic micropollutants (pharmaceuticals) in the final product (Simha *et al.*, 2021).

More than half of all pharmaceuticals consumed by humans end up in the urine, either in the form of a metabolite or as the parent compound (Lienert *et al.*, 2007). Previous research has indicated that organic micropollutants (OMPs) such as pharmaceuticals may end up in urine-derived fertiliser products, with the concentrations varying depending on the type of nutrient recovery process employed (Simha *et al.*, 2020a). Therefore, use of urine-derived fertiliser may generate concerns among users about OMPs reaching their food. For example, Tanoue *et al.* (2012) found that micropollutants can accumulate in plants (pea and cucumber) during use of organic manure and reclaimed wastewater in agriculture. Thus, it is imperative to remove micropollutants prior to using urine-derived fertiliser in agriculture (Simha *et al.*, 2021).

Treatment by membrane filtration (Pronk *et al.*, 2006), activated carbon filtration (Köpping *et al.*, 2020), electrochemical oxidation (Y Yang *et al.*, 2022) or ozonation (Escher *et al.*, 2006) are among the technologies reported to either reduce or remove pharmaceuticals from source-separated urine. However, all these processes have a high energy requirement or result in a by-product that may need further treatment before disposal (Larsen *et al.*, 2021b).

Ultraviolet (UV) treatment is a technology mostly employed for removal/destruction of micropollutants and for disinfection in drinking water treatment plants (Wols *et al.*, 2014). Treatment by UV radiation also has the potential to denature enzymes and remove pharmaceuticals from wastewater and urine (Zhang *et al.*, 2016b). Previous studies on degradation of OMPs in urine (Giannakis *et al.*, 2018; Zhang *et al.*, 2016a) have been limited in scope as regards number of compounds analysed. In addition, investigations of urease inactivation by UV have been limited to urease in water and in phosphate buffer (Clauß *et al.*, 2008; Luse *et al.*, 1963). Therefore, this thesis investigated UV treatment as an alternative treatment for urea-N stabilisation and for degradation of selected target OMPs, representing different therapeutic groups, in source-separated real urine from human subjects.

2. Aims and Structure

The overall aim of this thesis was to evaluate UV treatment as a stabilisation and organic micropollutant degradation method, to ensure safe nutrient recycling from source-separated human urine. Specific objectives were to:

- Investigate the effectiveness of UV treatment in inactivation of urease enzyme in source-separated human urine (Paper I)
- Evaluate the potential of the UV treatment in degradation of organic micropollutants (pharmaceuticals) in source-separated urine (Paper II)
- Determine the amount of electrical energy required to degrade >90% of organic micropollutants and reduce urease enzyme activity in source-separated human urine by >99% (Paper I and II).

3.Background

3.1. Sanitation around the globe

Sanitation, *i.e*. management of human excreta, has advanced from onsite excreta containment to establishment of centralised sewer systems serving large numbers of users (De Feo *et al.*, 2014; Matsui, 1997). Sanitation has gained much attention by governments worldwide since the perspective of economic growth has begun to involve human development, where sanitation is identified as basic human right (Rosenqvist *et al.*, 2016). However, with the current rapid rate of urbanisation around the world, technological advances in waste management are needed to meet the growing demand for sanitation (De Feo *et al.*, 2014).

Increasing awareness and acceptance of the term "sustainability" have paved the way for its adoption in sanitation and environmental work, leading to the birth of "ecological sanitation" (Esrey *et al.*, 1998). This has been accompanied by a shift in the perception of sanitation from a service to a resource (Larsen *et al.*, 1996). Viewing sanitation as a resource has revolutionised technologies at both household and industrial wastewater treatment (WWT) scale (Larsen *et al.*, 2021b). However, progress in implementation of such technologies has been very slow (Aliahmad *et al.*, 2023).

Although some progress has been made by countries around the world, realisation of the SDG-6.3 sub-target on water quality is now under question (Sadoff *et al.*, 2020). Globally, an estimated 360 billion m^3 of wastewater are generated annually of which 63% is collected (Jones *et al.*, 2021). However,

recent data on progress towards SDG-6 have revealed that only 58% of collected domestic wastewater is safely treated (UN, 2023). Despite the slow progress in realising SDG-6, technologies focusing on source separation and resource recovery are being implemented on a large scale. For instance, the city of Helsingborg in Sweden is implementing source separation to showcase the possibility for water savings and for efficient nutrient recovery by separating black water from grey water (Aliahmad *et al.*, 2023).

3.2. Source separation of urine

The fertiliser potential of urine has long been recognised (Jönsson *et al.*, 1999), but work on transforming this potential into usable fertiliser has made very slow progress (Aliahmad *et al.*, 2023). Ecological sanitation has brought a new perspective on the benefits of urine, attracting the attention of researchers (Larsen* *et al.*, 2009). Source separation is beneficial as it enhances nutrient recovery, minimises the micropollutant load and reduces health risks associated with faecal pathogens (Larsen *et al.*, 2021b; Vinnerås *et al.*, 2002). However, while source separation of urine appears to be ecologically relevant, Simha *et al.* (2017) emphasise the importance of careful monitoring when using source-separated urine for agricultural purposes, as it can lead to emissions of greenhouse gases (ammonia) and high acidity and salinity in agricultural soil.

Two types of urine-separating toilets have been developed, the urine diversion flush toilet (UDFT) and urine diversion dry toilet (UDDT) (Tilley *et al.*, 2014). Both of these toilet types separate urine from faeces, but their primary purpose is somewhat different. The UDDT is mainly designed to produce an odourless, fly-less faecal sludge product, whereas the UDFT is designed to collect urine with as little flush water as possible (Mcconville *et al.*, 2020). Separate collection of urine, in addition to saving flush water, could play a role in minimising water scarcity through use of the urine fraction for irrigation purposes (Jönsson *et al.*, 1999; Larsen *et al.*, 1996). A WHO (2006) report recommends that for safe use of urine for irrigation purposes, the urine must be kept in storage for at least six months. However, if the urine is not properly stored, the urea present will be hydrolysed to ammonia due to the action of urease, leading to loss of nitrogen as free

ammonia gas (Udert *et al.*, 2003a). Therefore, it is crucial to stabilise urine before employing any nutrient recovery process.

3.3. Urine stabilisation

Methods for stabilisation of urine mostly revolve around maintaining the nitrogen content in the urine, mainly urea-N (Senecal *et al.*, 2017). Before urine from a urine source separation system is dehydrated, it needs to be stabilised to prevent the urea being hydrolysed by free urease or urease-producing bacteria present in the system (Udert *et al.*, 2003a) (Figure 1). Without stabilisation, ammonia will leave the system in the form of gas, resulting in loss of nitrogen and contributing to greenhouse gas emissions (Simha *et al.*, 2017). Furthermore, hydrolysis and increased pH will give rise to a foul smell and production of settleable solids such as struvite and calcite that can block urine separation pipes (Udert *et al.*, 2003a).

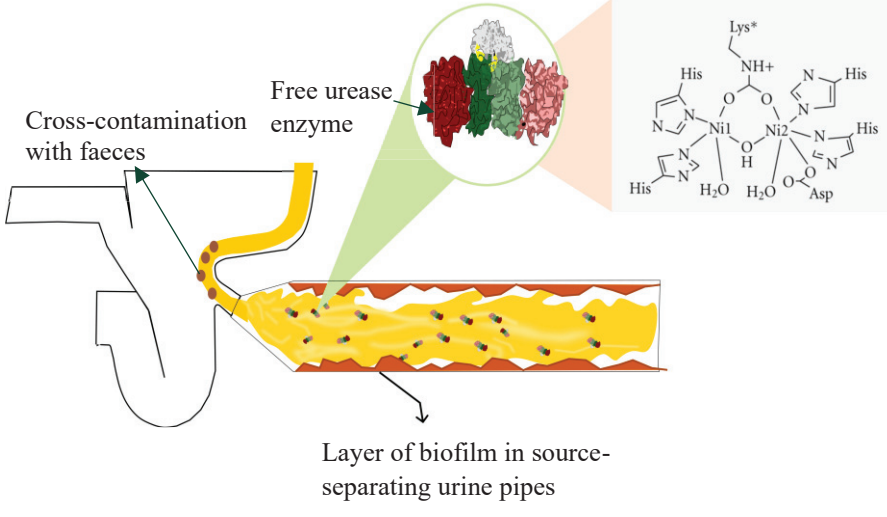

Figure 1. Presence of free urease and urease-producing bacteria as part of the biofilm created in source-separated urine collection pipes.

A recent review (Larsen *et al.* (2021b) compared technologies currently used to stabilise urine, including biological, chemical (acid and/or alkaline) and electrochemical stabilisation methods. Biological stabilisation methods,

unlike other stabilisation methods, promote microbial activity to convert urea-N into ammonium-nitrite and ammonium-nitrate (Udert *et al.*, 2012). However, the success of the process is highly dependent on the types of ammonium-oxidising microorganisms present and the process tends to produce a settleable solid that clogs collection pipes.

Chemical stabilisation methods are designed to halt the enzymatic action of both intracellular and extracellular urease. Alkaline urine stabilisation can be achieved by adding alkali oxides (*e.g*. NaOH and KOH) or alkaline earth hydroxides (*e.g*. $Mg(OH)_2$ and $Ca(OH)_2$). A study by Simha *et al.* (2020b) on different alkaline stabilisation media found that alkali oxides are completely soluble and alkaline earth hydroxides are sparingly soluble in urine solution. The alkaline earth hydroxides confer the advantage of stabilising urine for a long period, as they compensate for the pH buffering due to absorption of atmospheric CO_2 during open storage or drying of stabilised urine (Senecal-Smith, 2020). The best alkaline stabilisation method to use depends on the intended nutrient concentration pathway. If the nutrients are concentrated through reverse osmosis, then alkali oxide stabilisation is preferred. If nutrient concentration upon dehydration is required, stabilisation using alkaline earth hydroxides is recommended. For alkaline stabilisation to be effective, the pH must be kept higher than 10.5, as pH values below this threshold will reactivate urease, leading to urea hydrolysis (Geinzer, 2017), and as pH above 12 enables a storage time of more than 18 months (De Paepe *et al.*, 2020).

Acid stabilisation can be achieved by adding organic acids (*e.g*. citric acid and acetic acid) or inorganic acids (*e.g*. sulphuric acid, hydrochloric acid and phosphoric acid) (Maurer *et al.*, 2006; Ray *et al.*, 2018). Acid stabilisation is effective at pH less than 4, as otherwise urea may be hydrolysed by urease produced by microorganisms that can survive in low-pH environments (Mobley *et al.*, 1989; Simha *et al.*, 2023).

During drying of alkaline-stabilised urine, carbon dioxide is absorbed from the atmosphere, which lowers the pH of the system (Randall *et al.*, 2022; Senecal-Smith, 2020), necessitating close monitoring to maintain the pH. Drying of acid-stabilised urine, on the other hand, does not require close monitoring once a pH level less than 3 is attained (Simha *et al.*, 2023).

Examining inactivation of jack bean urease by heat and alkaline treatment found that urease is inactive at temperatures above 80 °C and pH above 13. The problem with using high temperature to inactivate the enzyme is that it will lead to thermal hydrolysis of urea (Geinzer, 2017; Randall *et al.*, 2022; Randall *et al.*, 2016).

Electrochemical stabilisation of urine involves altering the active site of urease activity through the action of reactive radicals (De Paepe *et al.*, 2020). The elevated pH (>11) attained in the electrochemical cell also deactivates the enzyme. However, this stabilisation method requires high energy inputs.

A rather fast and chemical-free alternative stabilisation technology is required to lengthen the storage time of urine and facilitate nutrient recovery. To this end, Clauß *et al.* (2008) investigated inactivation of urease using UV treatment and found that it can effectively inhibit the enzymatic action of urease. Furthermore, UV treatment has been shown to inactivate microorganisms in both urine and wastewater (Giannakis *et al.*, 2018).

3.4. Micropollutants in source-separated urine

Urine is a very complex matrix containing a number of organic and inorganic metabolic products (Putnam, 1971). In addition to natural metabolites, consumed pharmaceuticals end up in urine, in the form of parent compound and/or metabolites, *e.g*. Lienert *et al.* (2007) studied the excretion route of 212 pharmaceuticals and found that 64 ± 27% end up in urine. Thus source separation of urine requires separate treatment and control of such micropollutants, preventing them from reaching the environment.

A recent multinational survey (covering 16 countries) of consumer attitudes to consuming foods fertilised by urine-derived products found that the respondents were positive to consuming such foods (Simha *et al.* (2021). There were some concerns about health risks, but a considerable proportion of respondents believed that urine can be treated appropriately to minimise the risk (Simha *et al.* (2021). Presence of micropollutants or of pathogens from cross-contamination with faeces are the main reasons for consumer concerns about use of urine-derived fertilisers (Simha *et al.*, 2018). This concern may be justified, since in a pilot study conducted in Finland, pharmaceuticals were detected in a fertiliser made from concentrating an

alkaline-stabilised urine (Simha *et al.*, 2020a). Therefore, micropollutants must be removed prior to use of urine-derived fertiliser.

A number of technologies have been developed to separate or degrade the micropollutants in urine. Reviews by Maurer *et al.* (2006) and Larsen *et al.* (2021b) compared technologies for micropollutant separation and treatment and concluded that electrodialysis, nanofiltration and ammonia stripping are effective in separating micropollutants from nutrients. Ozonation, electrochemical oxidation and UV-based advanced oxidation processes (AOPs) are also reported to be effective in degradation of micropollutants from urine streams (Giannakis *et al.*, 2017; Zhang *et al.*, 2015). During separation of micropollutants in electrodialysis and nanofiltration, some nutrients such as ammonia and urea will be lost (Maurer *et al.*, 2006). On the other hand, oxidation processes such as ozonation are energy-intensive methods for removing micropollutants from urine and are associated with formation of toxic by-products (Larsen *et al.*, 2021b).

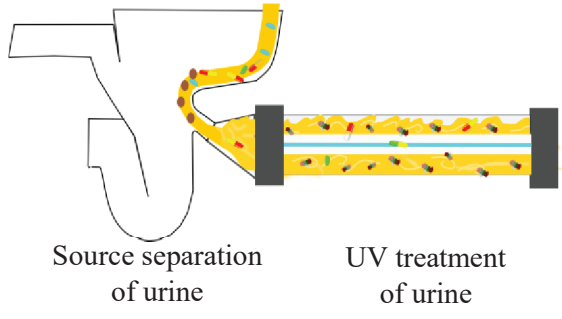

Figure 2. Ultraviolet (UV) treatment as a chemical-free method for nutrient stabilisation and organic micropollutant (OMP) degradation in OMP-contaminated source-separated urine.

Technologies such as electrochemical oxidation and UV treatment are multifunctional alternatives that can be used for both urine stabilisation and micropollutant degradation in urine (De Paepe *et al.*, 2020; Giannakis *et al.*, 2018; Maurer *et al.*, 2006). This thesis investigated the potential of UV treatment for urea-N stabilisation and OMP degradation in source-separated fresh human urine (Figure 2).

3.5. UV emission and mechanism of compound degradation

Technological development and application of UV treatment for different purposes began after the discovery of the bactericidal effect of sunlight (Downes *et al.*, 1877). Ultraviolet irradiation from UV lamps is generally classified based on the emission spectra as monochromatic, dichromatic or polychromatic (Miklos *et al.*, 2018). UV lamps are classified based on the pressure of the filler gas inside the lamp as low-pressure (0.01 to 0.001 mbar), medium-pressure (1 to 3 bar) and high-pressure (10 bar) (Masschelein *et al.*, 2016). The emission spectrum and different types of UV lamp technologies are presented in Figure 3.

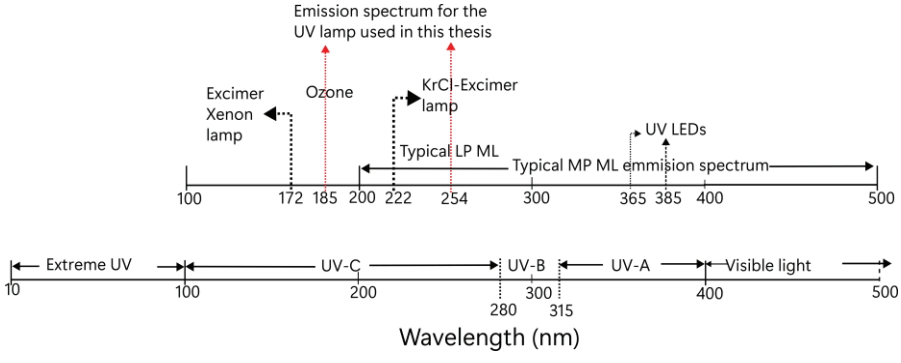

Figure 3. Emission spectrum for UV-A, UV-B and UV-C light. Typical emission spectrum for low-pressure (LP), medium-pressure (MP) mercury lamps, and specialized lamps; UV LEDs, KrCl and Xenon Excimer lamps. Ozone-generating LP and MP mercury lamps is shown by dashed arrow at 185 nm and 172 nm.

The most commonly used UV lamp is the low-pressure mercury lamp, which was used for drinking water and wastewater treatment in France and the USA in the early 20th century (Masschelein *et al.*, 2016). The emission spectrum of low-pressure mercury lamps is mainly concentrated in one or two wavelengths (185 and 254 nm, with 254 nm being the main spectrum). Medium-pressure lamps, on the other hand, have a wide emission spectrum, but the amount of photons emitted at most wavelengths does not exceed 10% of the main emission spectrum (Helios-quartz, 2023) (Figure 3).

However, the emission spectrum can be enhanced using different halide doping methods, which increase effective light emission across the spectrum and also change peak emission wavelength (Helios-quartz, 2023). For example, peak emission wavelength for a typical medium-pressure mercury lamp is 366 nm and this changes to 420 nm with gallium doping and to 298 nm, 357 nm and 420 nm when doping with lead (Helios-quartz, 2023). Specialist lamps, such as UV light-emitting diodes (LEDs) (Bhat *et al.*, 2023) and excimer lamps (Clauß *et al.*, 2008), are potential alternatives to mercury lamps for effective degradation of OMPs and enzyme inactivation (Figure 3).

Degradation of a compound subjected to UV irradiation depends on both the photochemical properties of the compound and the medium in which it is dissolved. Photochemical properties such as quantum yield (Φ) (mol of product formed per mol of photon absorbed) and molar absorption coefficient (ε) (absorbance of photon emitted at a given wavelength) determine the extent of degradation by direct photolysis (Parsons, 2004). In order for photodegradation to occur, a compound must have an atom with a double or triple bond, or with a lone pair of atoms, so that the absorbed electrons can be moved from a bonding or non-bonding orbital to an anti-bonding orbital (Masschelein *et al.*, 2016). Double and triple bonds are generally found in compounds with an aromatic functional group and bonds formed by nitrogen, oxygen and members of the halogen group.

Aromatic compounds can be degraded through isomerisation, cycloaddition, hydrogen abstraction, dimerisation, electrocyclisation, substitution and rearrangement reactions (Dinda, 2017). These degradation mechanisms apply in addition to deamination, decarboxylation and ring cleavage for OMPs such as pharmaceuticals (Ahmad *et al.*, 2016). Most OMPs and amino acid residues of urease, such as histidine and tryptophan, contain aromatic groups which are susceptible to photodegradation (Luse *et al.*, 1963; Wypych, 2020). It should be noted that the amount of absorbed energy must exceed the energy required to break the bonds. For instance, deamination of ethylamine may require 324 KJ mol^{-1}, which is equivalent to energy emitted at a threshold wavelength of 370 nm. Therefore, energy higher than the bond

energy increases the chance of breakage, even if the matrix is somewhat different (Pelayo *et al.*, 2023).

Ultraviolet lamps emitting photons at lower wavelength (<200 nm) can photolyse water to produce hydroxyl radicals (OH•) and hydrogen atoms (H•) (Zoschke *et al.*, 2014), enhancing degradation even more. Hydroxyl radicals and hydrogen atoms can both react with organic compounds non-selectively, *e.g.* OH• reacts with diclofenac with a rate constant of 8.2 $x10^9$ $M^{-1}s^{-1}$ (Wols *et al.*, 2014) and with cysteine with a rate constant of 2.4 $x10^9$ $M^{-1}s^{-1}$ (Enescu *et al.*, 2006).

4.Methodology

4.1. Urine collection and characterisation

Fresh urine donations from male and female volunteers (aged 20-65) were collected in high-density polyethylene (HDPE) bottles. The collected urine from different individuals was pooled and mixed before use. Pooled urine was cold-stored at 4 °C for <4 h prior to use (Paper I) or for one day prior to use (Paper II). The fresh urine batches were then allowed to equilibrate to room temperature (20 ± 2 °C) before the experiment. Synthetic fresh urine was prepared using a recipe developed by Ray *et al.* (2018), but without urea (Paper I). Milli-Q water was used as a control medium in parallel to real urine (Papers I & II). When used hereafter in this thesis, the term 'real urine' refers to real fresh human urine and the term 'synthetic urine' refers to synthetic fresh urine without urea.

Urine was analysed for pH (Accumet AE150; Fisher Scientific, USA), electrical conductivity (EC) (Cond 340i multimeter; WTW, Germany), total solids (TS) (105 °C for 24 h) and volatile solids (VS) (650 °C for 6 h in a furnace (LH30/12; Nabertherm GmBH, Germany).

Ammonium nitrogen (NH_4-N), total nitrogen (N_{tot}) and chemical oxygen demand (COD) were determined colorimetrically using Spectroquant® test kits (Merck KGaA, Darmstadt, Germany) in a photometer (NOVA 60 A, Merck KgaA, Germany). Calcium (Ca), potassium (K), magnesium (Mg) and phosphorus (P) concentrations in fresh urine were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), using an Avio® 200 spectrophotometer (PerkinElmer, USA).

Ultraviolet absorbance was measured to determine the light absorbance of each matrix in the wavelength range between 190 and 400 nm, using a Lambda 365 UV-vis spectrophotometer, 1 cm path length (Perkin-Elmer, USA).

4.2. Photoreactor set-up

The photoreactor set-up consisted of a 15 W low-pressure tubular mercury UV lamp (Heraeus, 2022) emitting light predominantly at 254 nm and 185 nm, a quartz sleeve and a cylindrical chamber (40 cm length, 3.7 cm diameter). Urine (synthetic or real) or water was circulated using a peristaltic pump (Masterflex, Fisher Scientific, USA) at a rate of 40 mL min^{-1} (Figure 4).

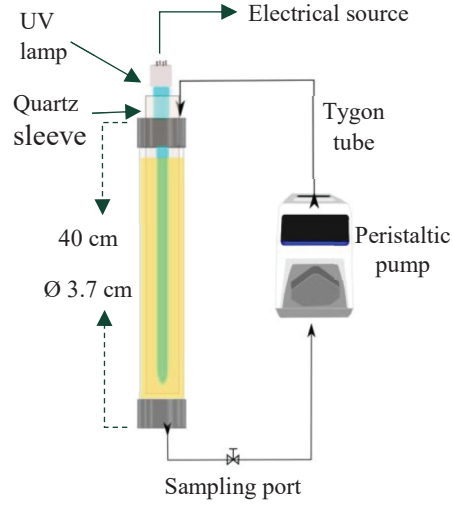

Figure 4. Photoreactor used for ultraviolet (UV) treatment, consisting of a low-pressure mercury lamp (185 and 254 nm) surrounded by a quartz sleeve, which was connected to a peristaltic pump to recirculate the sample through the photoreactor.

4.3. Experimental procedure

4.3.1. UV treatment for inactivation of urease (Paper I)

The photoreactor was used to evaluate photoinactivation of jack bean (*Canavalia ensiformis*) urease (activity of ≥5 U mg^{-1}; Merck, Germany) in Milli-Q water, synthetic urine (without urea) and real fresh human urine. Urease was spiked at a concentration of 500 mg L^{-1} to each matrix. The matrices were then subjected to 0.4, 1.3, 3.3, 7.1, 16.5, 35 and 71 min of UV irradiation, which is equivalent to theoretical UV fluence of 10, 35, 85, 185, 435, 935 and 1935 J m^{-2}. These UV irradiation times were determined based on the time the matrices spent in the photoreactor, excluding the recirculating pipes. Urea solution (10 g L^{-1}) was added to the UV-treated samples and EC value was used to detect and quantify urease activity 0.5, 1, 2, 4, and 8 h after treatment.

Control experiments were conducted in the absence of UV light, but with all other experimental conditions identical to those in the main experiments. To compensate for the temperature difference between the UV and UV-free control experiments, an empirical relationship was developed in a separate experiment for conductivity differences caused by temperature rise inside the photoreactor. A standard curve for the relationship of EC with urea hydrolysis was developed from UV-free control experiments through measurement of NH_4-N concentrations, and the empirical equation was used to estimate enzymatic activity for the UV-treated samples.

4.3.2. UV treatment for micropollutant degradation (Paper II)

Micropollutants were added at a concentration of 60 µg L^{-1} to one-day-old real urine and water, which were then UV-irradiated in the photoreactor for a treatment time of 1, 2.5, 5, 10, 20, 40 and 80 min, which is equivalent to theoretical UV fluence of 26, 65, 130, 260, 520, 1030 and 2060 J m^{-2}.

Solid phase extraction (SPE) of micropollutants from samples was performed using Oasis HLB cartridges (6 mL, 150 mg sorbent, 60 µm). After loading 5 mL internal standard solution to 5 mL sample, conditioning was performed using 5 mL methanol and 5 mL MilliQ water. Samples were then

concentrated using nitrogen gas. Finally, 800 µL Milli-Q water were added to the concentrated samples to make them up a final volume of 1 mL. The samples were stored in the freezer (-20 °C) in 7 mL amber vials until further use. Concentrations of micropollutants in samples were analysed using a DIONEX UltiMate 3000 ultra-high pressure liquid chromatography (UHPLC) system (Thermo Scientific, Waltham, MA, USA) coupled to a triple quadrupole mass spectrometer (MS/MS) (TSQ QUANTIVA; Thermo Scientific, Waltham, MA, USA).

Linearity of calibration samples was within the range 0.9614-0.9998 and limit of quantification (LOQ) was within the range 0.01-5.5 µg L^{-1}. The average recovery of OMPs in methanol was 90±16%. There were no contaminants in blank samples and MilliQ water. Concentrations higher than the spiked amount were detected for sebacic acid, sertraline, caffeine, sulisobenzone, nicotine, methylparaben and budesonide in fresh urine samples.

Control experiments were conducted in the same photoreactor, but without UV irradiation and with samples taken at fewer time points (1, 10 and 80 min). Sample processing and storage followed the same procedure as UV-treated samples.

4.4. Calculation of photoinactivation and photodegradation

4.4.1. Enzyme inactivation kinetics (Paper I)

According to Ray *et al.* (2018), hydrolysis of urea in human urine can be characterised by measurement of EC. Thus, empirical questions were developed by relating measured EC values to enzymatic activity from UV-free control experiments. Measured TAN was converted into enzymatic activity using equation:

$$Enzymatic\ activity\ (EA) = \frac{C_{TAN}}{MM_n} \times \frac{1}{X \times t} \qquad (1)$$

where C_{TAN} is concentration of total ammonia nitrogen (TAN, mg L^{-1}) in solution, MM_n is molar mass of NH_4 (mg $mmol^{-1}$), X is concentration of urease (mg_u L^{-1}) and t is time (min).

Rate constant for urea hydrolysis were calculated by fitting the plot of experimentally determined concentration of TAN and time with pseudo-zero order kinetics, using equation:

$$C_t = C_0 + k \times t \qquad (2)$$

where C_0 and C_t is initial and final concentration, respectively, of TAN (mmol mg_u^{-1}) at any time t (min) and k is the rate constant (mmol TAN mg_u^{-1} min^{-1}) for enzymatic urea hydrolysis.

Relative enzymatic activity (REA, %) was calculated as the ratio of enzymatic rate constant in presence of UV (k_{UV}, mmol TAN mg_u^{-1} min^{-1}) to enzymatic rate constant in absence of UV (k_C, mmol TAN $mg_u^{-1}min^{-1}$) for all three matrices:

$$Relative\ Enzymatic\ Activity\ (REA) = \frac{k_{UV}}{k_C} \times 100 \qquad (3)$$

where K_{UV} and K_C *is the* rate constant for UV-treated samples and UV-free control samples, respectively.

Since real fresh urine naturally contains urea, enzymatic urea hydrolysis occurred in the photoreactor during UV treatment. During calculation of relative enzymatic activity, urea hydrolysis timewas considered, *e.g.* enzymatic activity in urine samples receiving 7 min of UV irradiation was compared with enzymatic activity during 7 min in urine without UV irradiation, *i.e*. in the UV-free control experiment.

4.4.2. Micropollutant degradation kinetics (Paper II)

Degradation of spiked OMPs in both water and real urine due to UV treatment was calculated as:

$$Degradation(\%) = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \qquad (4)$$

where C_0 and C_t is initial and post-treatment (sampling time) concentration of OMP (µg L^{-1}), respectively.

Rate constant of OMP degradation was determined experimentally by plotting each OMP concentration against UV fluence/irradiation time and fitting to the pseudo-first order rate equation:

$$ln\left(\frac{C_t}{C_0}\right) = -kt_e \quad (5)$$

where t_e (min^{-1}) is UV irradiance time and k is the degradation rate constant min^{-1}).

The amount of electrical energy required to degrade 50% (UV_{t50}) and 90% (UV_{t90}) of the initial concentration of OMPs was calculated according to Eq. 6 and Eq. 7, respectively:

$$UVe_{50} = \frac{ln2}{k} \quad (6)$$

$$UVe_{90} = \frac{ln(0.1)}{k} \quad (7)$$

4.5. Statistical analysis

Two-way analysis of variance (ANOVA) with 95% confidence interval was conducted using R statistical software (version 4.1.2) and RStudio version 2022.02.3, to examine the effects of matrix and UV irradiation time on urease enzymatic activity (Paper I) and degradation of micropollutants (Paper II). Assumptions in ANOVA were tested using residual analysis. The box plot method was used to identify outliers, the Shapiro-Wilk test to assess the normality assumption and Levene's test to assess homogeneity of variances. There were no extreme outliers in either the enzyme inactivation or micropollutant degradation data. Residuals of data points in enzyme inactivation data were normally distributed, but residuals of data points in micropollutant degradation data had to be log-transformed to satisfy the normality assumption. Homogeneity of variances was found for all matrices in both studies. Pairwise comparisons on group level of main effects were analysed using Tukey's post-hoc test.

5. Results

5.1. Photo-inactivation of urease (Paper I)

The effect of UV treatment on enzymatic activity of urease in fresh urine, synthetic urine (without urea) and MilliQ water were assessed based on EC measurements, which were used to track enzymatic activity for 30, 60 and 120 min after UV treatment.

Enzymatic activity was similar in the UV-free control treatment of both MilliQ water and synthetic urine ($3.2x10^{-3}$ and $3.3x10^{-3}$ mmol TAN mg_u^{-1} min^{-1}, respectively) (Figure 5a). However, enzymatic activity was slower in the UV-free control treatment of fresh human urine ($2.0x10^{-3}$ mmol TAN mg_u^{-1} min^{-1}).

When using UV treatment to inactivate urease, there was an effect of matrix on enzymatic activity (Figure 5). Synthetic urine and MilliQ water had highly reduced activity ($8.0x10^{-8}$ and $5.0x10^{-5}$ mmol TAN mg_u^{-1} min^{-1}, respectively) following UV irradiation for 1.3 min. For fresh urine, a longer UV irradiation time (35 min) was needed to reduce enzymatic activity to $1.0x10^{-4}$ mmol TAN mg_u^{-1} min^{-1} (Table 1).

The fresh urine already contained urea, which was hydrolysed while the urease-spiked real urine was being UV-treated. Urea hydrolysis was high until the fresh urine was exposed to UV irradiation time of 71 min, after which enzyme activity was below the detection limit (Figure 5b). The higher ammonia formation during UV treatment of urine compared with the UV-

free control was most likely due to the higher temperature inside the reactor (35±1 °C) compared with the UV-free control (22±1 °C) (Figure 5b; Paper I).

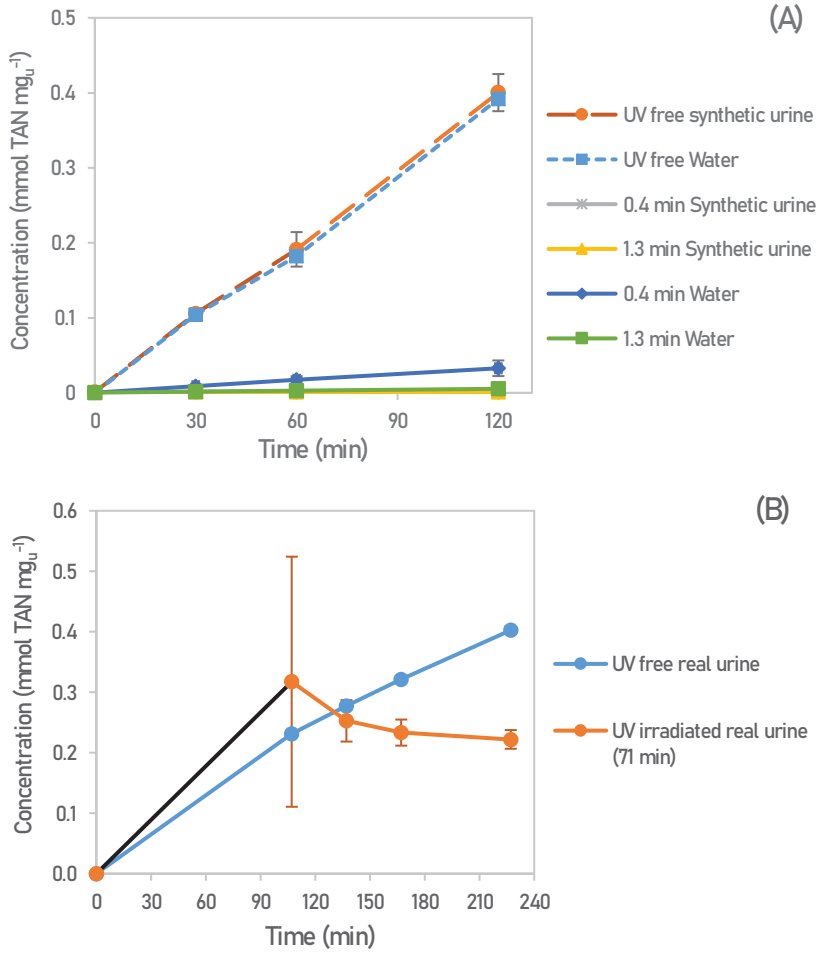

Figure 5. Concentration of total ammonia nitrogen (TAN) in ultraviolet (UV)-free and UV-irradiated (A) water and synthetic urine (without urea) exposed to UV irradiation for 0.4 and 1.3 min and (B) real urine exposed to UV irradiation for 71 min. Black line and orange line represents urea hydrolysis in real urine during UV treatment and after treatment, respectively.

Enzymatic activity was observed to decrease as UV irradiation time increased for all matrices. However, UV irradiance for only 0.4 min was required to reduce relative enzymatic activity down to 1% in synthetic urine and 9% in water, whereas the same duration of irradiance did not affect enzyme performance at all in real urine (Table 1). With an UV irradiation time of 3.3 min, enzymatic activity was below the detection limit for water and synthetic urine, while relative enzymatic activity in real fresh urine was only reduced by 20%.

Table 1. *Enzymatic rate constant k (mmol mg_u^{-1} min^{-1}) for total ammonia nitrogen (TAN) formation in water, synthetic urine (without urea) and real urine subjected to different levels of ultraviolet (UV) irradiation using a low-pressure mercury lamp (185 and 254 nm)*

UV irradiation time (min)	During UV treatment	After UV treatment		
	Urine	Real urine	Synthetic urine	Milli-Q water
0		2.0×10^{-3}	3.3×10^{-3}	3.2×10^{-3}
0.4	4.4×10^{-3}	2.0×10^{-3}	2.0×10^{-5}	3.0×10^{-4}
1.3	4.5×10^{-3}	1.7×10^{-3}	8.0×10^{-8}	5.0×10^{-5}
3.3	4.6×10^{-3}	1.6×10^{-3}	0.0	5.0×10^{-6}
7	4.4×10^{-3}	1.2×10^{-3}	0.0	0.0
16.5	3.9×10^{-3}	9.0×10^{-4}	0.0	0.0
35	4.1×10^{-3}	1.0×10^{-4}	0.0	0.0
71	3.0×10^{-3}	0.0	0.0	0.0

Urease enzyme activity reached below detection limit in real urine with irradiation time of 71 min (Table 1). This is equivalent to an electrical energy demand of ≈ 60 kWh m^{-3} for treating one cubic meter of real urine which is 21 fold and 52 fold higher than water and synthetic urine counter parts respectively (Figure 6).

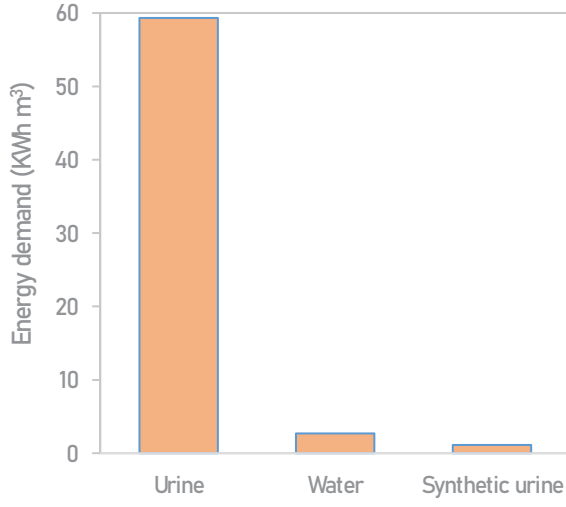

Figure 6. Electrical energy demand (kWh m^{-3}) to reduce >99% of urease activity in real urine, water and synthetic urine (without urea) by UV photoinactivation using a 15 W low-pressure mercury lamp (185 nm and 254 nm) with a fluence of 0.43 µW m^{-2}. For all matrices, the initial concentration of urease is 500 mg L^{-1} (2500 AU L^{-1}).

5.2. Photodegradation of OMPs (Paper II)

Degradation of 75 OMPs in water and real fresh urine subjected to different level of UV irradiation was investigated. In UV-free controls of water, nine compounds (atorvastatin, clopidogrel, encazamene, tamoxifen, simvastatin, ioperamide, meclofenamic acid, mefenamic acid and valsartan) showed more than 50% degradation over 80 min (see SI in Paper II). In UV-free controls of urine, however, only three compounds (clopidogrel, encazamene and tamoxifen) showed more than 50% degradation with a treatment time of 80 min (SI in Paper II).

During UV treatment of water, more than 99% degradation within 1 min of treatment was observed for 18 out of 75 target OMPs and half-life of 72 out of 75 OMPs was reached within 10 min of UV irradiation. The average degree of degradation of OMPs in water after 1, 2.5 and 5 min of UV

irradiation was 75% (±30%), 82% (±27%) and 93% (±17%), respectively (SI in Paper II).

During UV treatment of urine, only 18 out of the 75 OMPs showed a half-life of less than 20 min and the average degree of OMP degradation with UV irradiance time of 5, 20 and 80 min was <15% (±15%), <30% (±24%) and 55% (±36%), respectively (SI in Paper II). The target OMPs also showed different degrees of degradation, even when they belonged to the same therapeutic class, *e.g.* diclofenac and tramadol (Figure 7, left-hand axis). Fast degradation within 1 min of UV irradiation was observed for OMPs such as diclofenac and sulfamethoxazole, while persistence was observed for metoprolol and clarithromycin (Figure 7).

When determining the amount of energy required to degrade the OMPs in both media (water and real urine), only OMPS categorised as contaminants of emerging concern (Patel *et al.*, 2019) were considered. The amount of UV irradiation required to degrade more than 90% of the initial concentration differed for different OMPs (Figure 7, right-hand axis). For example, in both real urine and water, diclofenac required less energy than clarithromycin (Figure 7).

In general, <10 min and >500 min of UV irradiation was required to degrade >90% of the initial concentration of OMPS in water and real urine, respectively. The energy requirement for degradation of 14 OMPs, *e.g.* trimethoprim, in urine could not be calculated, as their degradation could not be modelled using pseudo first-order kinetics (Figure 7). It should be noted that energy losses in the set-up were not considered during estimation of energy requirement, and therefore actual energy demand may differ in different settings or set-ups.

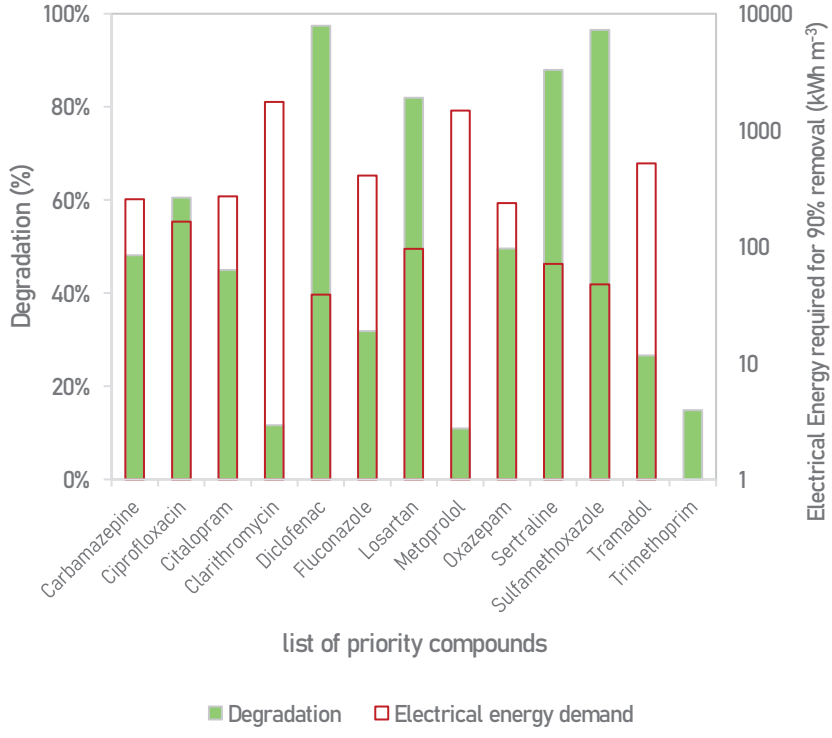

Figure 7. (Left hand axis) Degradation of organic micropollutants (OMPs) categorised as contaminants of emerging concern when subjected to ultraviolet (UV) irradiation for 80 min by 15 W low pressure mercury lamp (185 nm and 254 nm) (represented by green bars) and (right hand axis) amount of electrical energy required to degrade 90% of the initial concentration, represented by log scale (hollow bars).

5.2.1. Degradation kinetics of OMPs

Different degradation trends were observed for the target OMPs. Figure 8 shows the response of clopidogrel, memantine, sulfamethoxazole and venlafaxine (OMPs representing different therapeutic classes) in water and urine to UV treatment. Clopidogrel showed >90% degradation in UV-free controls of both urine and water, which was similar to the response of tamoxifen and encazamene (Figure 8; SI in Paper II). Except for memantine and two others, the OMPs followed similar degradation trends to

sulfamethoxazole and clopidogrel during UV treatment of water (Figure 8b). Memantine and venlafaxine in urine were persistent during UV treatment (<5% degradation), as seen for degradation of 14 other OMPs in urine (Figure 7a,7d).

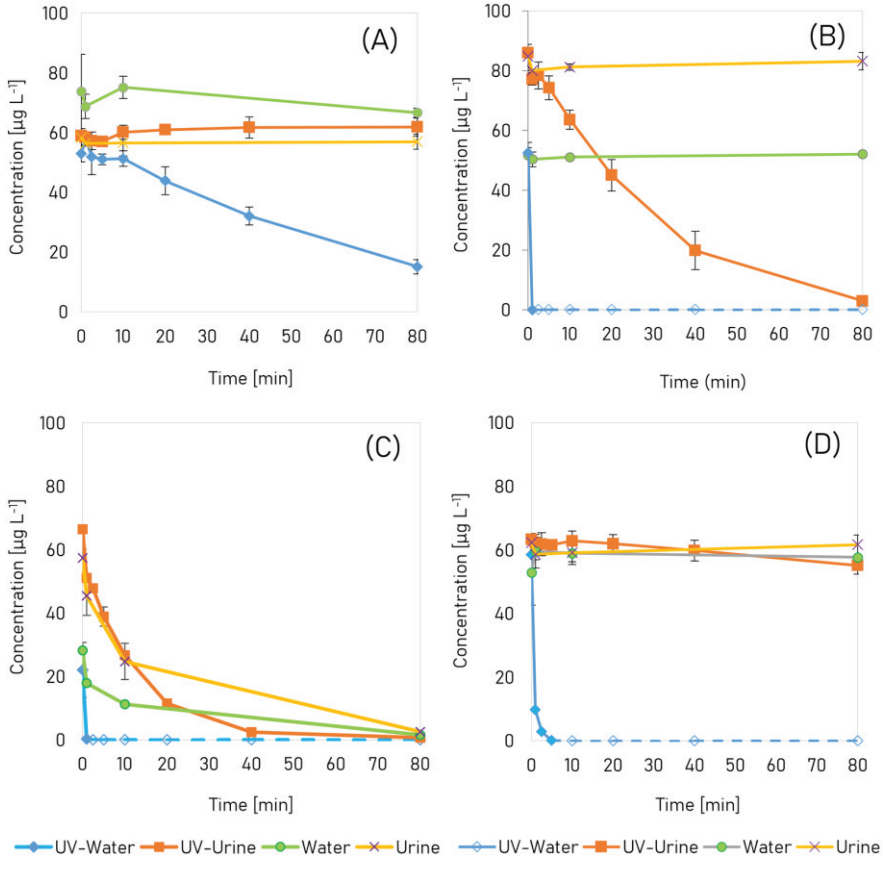

Figure 8. Degradation kinetics of (a) memantine, (b) sulfamethoxazole, (c) clopidogrel and (d) venlafaxine in water and fresh urine, with and without ultraviolet (UV) irradiation using a 15 W low-pressure mercury lamp (185 nm and 254 nm). The open diamonds in panels b, c and d indicate that these micropollutants were present in concentrations below the limit of quantification (LOQ).

6. Discussion

6.1. Photo-induced degradation of OMPs and inactivation of urease

The effect of UV radiation on target compounds obeys the second law of photochemistry, which states "If a molecule absorbs radiation, then one molecule is excited for each quantum of radiation absorbed" (Wypych, 2020). This means that for a given compound to absorb a photon, the following conditions must be satisfied: (i) the compound must contain chromophores which receive the photon and (ii) the incoming photon energy must match the energy required by the bonds of chromophores. Dissipation of the absorbed energy makes a compound degrade or an enzyme deactivate, *i.e.* the absorbed energy must be dissipated by rotation or cleavage of bonds, and/or become activation energy to start a reaction with other molecules (Wypych, 2020). For compounds exhibiting such characteristics, degradation can be predicted by two photochemical properties, molar extinction coefficient (ε) and quantum yield (Φ) (Yu *et al.*, 2019).

Degradation of OMPs will therefore differ from compound to compound, depending on the photochemical properties (SI in Paper II). The UV-vis results for MilliQ water showed that pure water does not absorb light at 254 nm wavelength and that photons emitted at this wavelength are absorbed by the OMPs (Figure 9; SI in Paper II). Moreover, urease-spiked water and synthetic urine (without urea) showed very low absorbance at 254 nm compared with real urine, and therefore the photons at this wavelength are absorbed by urease (Figure 9). However, due to differences in the photochemical properties of OMPs (ε and Φ), degradation through direct photolysis differed (Table 2)(Wols *et al.*, 2014). For example, based on predicted degradation of diclofenac (97%) and mefenamic acid (73%),

photolysis was responsible for around 92% and 4% of the degradation, respectively (Table 2) (Wols *et al.*, 2012).

Micropollutants absorb UV light over a wide range of wavelengths. The absorbance for the cocktail of OMPs studied in this thesis was within the wavelength range 190-300 nm, and the absorbance increased drastically when the wavelength decreased from 250 nm to 190 nm (Figure 9). During direct photolysis, the absorbed photons forced the OMPs to undergo different degradation mechanisms. For example, deamination, decarboxylation, dehalogenation and photo-induced ring cleavage occur due to the presence of main functional groups like amines, carboxylic acids, halide and benzene groups that can absorb photons (Ahmad *et al.*, 2016).

Inactivation of enzymes follows somewhat similar degradation routes, where chromophores or photo-susceptible functional groups absorb photons and undergo degradation by the above-mentioned routes or by structural changes (Saha *et al.*, 1995). A difference for enzyme deactivation compared with OMP degradation is that enzymes tend to have a conformational structure that changes upon receiving photons, eliminating their activity without losing a functional group (Luse *et al.*, 1963). The amino acid residues that make up urease (*e.g*. histidine, cysteine and tryptophan) contain peptide bonds with the capability of absorbing light in the range 180-230 nm and at 254 nm (Beaven *et al.*, 1952). When these amino acids absorb light, amine and carboxyl functional groups are cleaved off, a process commonly known as deamination and decarboxylation (Clauß *et al*., 2008; Luse *et al*., 1963).

Previous studies by Landen (1940) and Beaven *et al.* (1952) showed that enzyme inactivation depends on ε and Φ, and that UV absorbance increases with increasing radiation intensity (<254 nm). Quantum yield of 0.0008 and 0.0098 has been reported at wavelength of 313 nm and 186 nm, respectively, *i.e*. it is 10-fold higher at lower wavelengths (Landen, 1940). Furthermore, Beaven *et al.* (1952) reported a six-fold and two-fold increase in molar extinction coefficient for cysteine and tryptophan, respectively, where ε increased from 10 $M^{-1}cm^{-1}$ at 260 nm to 60 $M^{-1}cm^{-1}$ at 230 nm for cysteine and from 1.9×10^{-3} $M^{-1}cm^{-1}$ at 242 nm to 33.5×10^{-3} $M^{-1}cm^{-1}$ at 218 nm. Although independent UV absorbance measurements of amino acids were not performed in this thesis, the UV-vis absorption results revealed that

absorbance of the enzyme as a whole increases as the wavelength decreases (Figure 9).

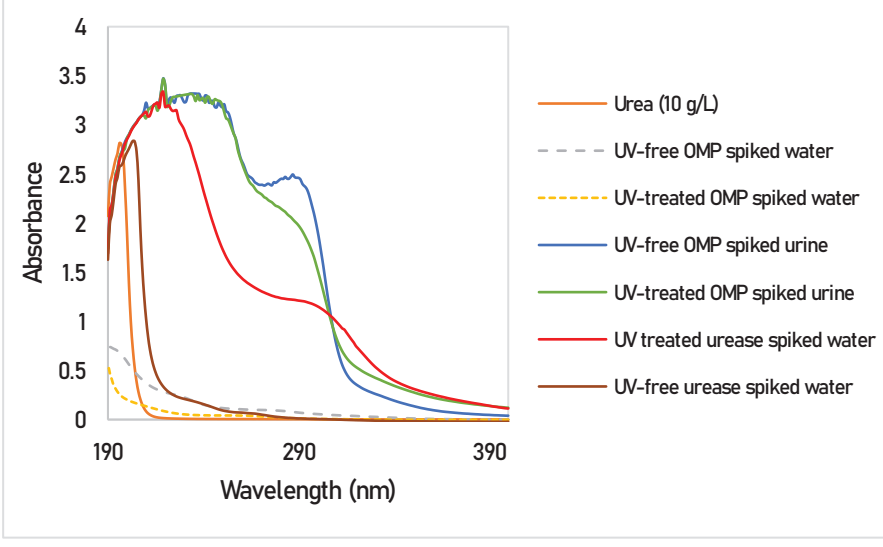

Figure 9. Ultraviolet (UV) light absorbance curve of UV-free and UV-treated samples of water and urine spiked with urease (500 mg L^{-1}) and a cocktail of organic micropollutants (OMPs) (each at 60 µg L^{-1} or 18 µg absolute mass). UV-treated samples of urease-spiked and OMP-spiked solutions received 71 min and 80 min of UV irradiation, respectively, using a 15 W low-pressure mercury lamp (185 nm and 254 nm). Solution of urea with a concentration of 10 g L^{-1}. All samples except OMP-spiked water were diluted (10-fold) with Milli-Q water prior to measurement.

Due to higher molar extinction coefficient of urease enzyme at lower wavelengths (<200 nm), use of low-pressure mercury lamps that emit light at 185 nm will inactivate urease faster than inactivation at 254 nm (Landen, 1940). A study which investigated inactivation of urease enzyme in distilled water using low-pressure mercury lamps emitting light at 254 nm found that the enzyme retained more than 80% of its activity after UV treatment (4000 J m^{-2}) (Clauß *et al.*, 2008). In this thesis, enzymatic activity was below the detection limit with UV irradiation time of 1.3 and 3.3 min, which is equivalent to UV fluence of 85 J m^{-2} and 35 J m^{-2} in water and synthetic fresh urine (without urea), respectively. The faster inactivation of urease in this thesis can be attributed to the use of UV lamps emitting light at lower

wavelength (185 nm), which enhanced the molar extinction coefficient and thus resulted in faster inactivation (Clauß *et al.*, 2008; Landen, 1940).

6.2. Photo-oxidative degradation of OMPs and inactivation of enzyme

As explained in section 6.1, degradation of OMPs by photolysis depends on their photochemical properties, but overall degradation of OMPs does not rely solely on photolysis, but also on photooxidation. The low-pressure mercury lamp used in this thesis emits light at 185 nm and can photolyse water molecules to generate hydroxyl radicals (OH•) that react with organic materials instantaneously (Zoschke *et al.*, 2014). Hydroxyl radicals are known for their non-selective reaction with organic compounds (Wols *et al.*, 2012; Yu *et al.*, 2019). For a compound with low molar absorption and quantum yield, the reactivity to OH• will be important for degradation (Wols *et al.*, 2012).

Yu *et al.* (2019) divided OMPs into three categories depending on their photo-reactivity and reactivity to OH•. They classified OMPs such as diclofenac and sulfamethoxazole as highly photo-reactive; fluoxetine and HCTZ as moderately photo-reactive; and carbamazepine and trimethoprim as photo-persistent. Wols *et al.* (2014) predicted degradation of OMPs in a typical water matrix (1.78 mg L^{-1} DOC and pH 8) by UV treatment (4000 J m^{-2}) using a low-pressure mercury lamp emitting light at 254 nm and observed actual degradation of those OMPs, supporting findings by Yu *et al.* (2019). Comparable results were obtained in Paper II, where diclofenac and sulfamethoxazole in water were degraded very rapidly (by <1 min of treatment), while carbamazepine and trimethoprim in urine were persistent to UV treatment (Table 2).

High degradation of OMPs in water was achieved in Paper II compared with results reported by Wols *et al.* (2014), indicating that both photolysis and photo oxidation likely occurred in the system (*e.g.* for metoprolol, primidone and trimethoprim) (Table 2). However, in a different matrix (*e.g.* wastewater effluent), OMP degradation will be dominated by photo-oxidation as there will be second-order reactions with radicals other than OH•, HCO_3• and SO_4• (Zhang *et al.*, 2015).

Correlation test was conducted to test for associations between photo-susceptible functional groups, photochemical properties (ε and Φ), physicochemical properties (Log Kow and pKa) and rate of hydroxyl radical ($K_{OH\bullet}$) are related with degradation of OMPs in either matrix (urine or water). The results revealed that there was no significant correlation (p>0.05) between presence of photoactive functional group/s, physicochemical and physicochemical properties of an OMP and degradation of the OMP in either of the matrices (SI in Paper II). However, correlation tests on a subset of OMPs (therapeutic groups) to check for associations between degradation and photochemical properties revealed that only antihypertensive compounds such as atenelol and metoprolol showed a strong positive correlation with $K_{OH\bullet}$ and strong negative correlation with molar absorption (ε) (SI in Paper II). This indicates that these compounds were degraded to a larger extent by photooxidation rather than photolysis. (Wols *et al.*, 2014) predicted degradation of metoprolol to be ≈60%, with photolysis only contributing to ≈4% of total degradation.

Photo-oxidative inactivation of enzymes occurs when an oxidant such as OH• reacts with the outer part of the enzyme, which is susceptible to oxidation (Saha *et al*., 1995). Reaction of hydroxyl radicals with either of the amino acids of urease will bring about conformational change by adding or abstracting a hydrogen atom, which leads to chemical modification of the active site (Buxton *et al*., 1988; Villamena, 2013). Inactivation by oxidation is a two-step process, where the first step involves bringing amino acids residing in the middle of the enzyme to the surface and the second step involves conformation change due to oxidation of thiol groups, which alter S-S bridges, RSOH or RSO_2H groups of susceptible amino acids (Krajewska, 2011; Mozhaev *et al.*, 1982). Involvement of inorganic ions like Na^+, K^+, Ca^{2+} and Mg^{2+} is not well understood, but it is reported that they may take part in peptide bond breakage due to oxidation of protein radicals (Saha *et al*., 1995). Krajewska (2011) reported that the thiol groups on urease are prone to oxidative damage.

Addition of salts of metals such as NaCl, NaH_2PO_4 and Na_2SO_4 may give rise to formation of radicals such as $Cl^-\bullet$, $SO_4^{2-}\bullet$, $PO_4^{2-}\bullet$, which contribute to oxidative damage during UV treatment of synthetic fresh urine (Neta *et al.*,

1988). Faster inactivation of urease in synthetic urine than in water might be attributable to presence of inorganic ions (Figure 5).

6.3. Degradation of OMPs and inactivation of enzyme in real fresh urine

Urine is a very complex solution containing inorganic ions, hundreds of metabolites and organic substances (Bouatra *et al.*, 2013). Urea, creatinine, phenols, hippuric acids and citric acid are among the organic compounds present in high concentrations (1-23 g L^{-1}) in urine, while chlorides, sodium potassium and ammonia are among the inorganic compounds found in low concentration (750-1800 mg L^{-1}) (Putnam, 1971). Because of the presence of both organic (COD >10 g L^{-1}) and inorganic compounds, inner shielding occurs all the way from 190 nm to 400 nm (Figure 9), thus reducing the degradability of OMPs by direct photolysis (Doll *et al.*, 2003). This is reflected in the lower degradation of OMPs in urine (55±36%) than in water (99±4%) in Paper II.

A study by Zhang *et al.* (2015) of UV-induced degradation of pharmaceuticals using a low-pressure UV lamp found that components of synthetic urine (urea and inorganic salts) do not have a significant effect on the photolytic degradation of pharmaceuticals, since their absorbance is minimal at 254 nm. Therefore, organic compounds apparently prevent UV light from reaching the OMPs. If there were no interference of organics with UV, >99% inactivation of urease and >95% degradation of OMPs in real urine would have been achieved with UV irradiance of 3.3 and 10 min, respectively.

Although high energy was required to treat OMP-spiked urine, a COD reduction of 19% was observed upon UV irradiance for 80 min (SI in Paper II). In addition, the concentration of urea and ammonium decreased by 19% and 20%, respectively, indicating oxidation of urea (SI in Paper II). Another process that potentially inhibits both OMP degradation and enzyme inactivation is scavenging of OH• by organic materials (Buxton *et al.*, 1988; Zhang *et al.*, 2015).

Table 2. *Photochemical properties of selected organic micropollutants (OMPs) and their degradation in OMP spiked water and real fresh urine*

Type of OMP	ε ($M^{-1}cm^{-1}$)[a] x10^3	Φ (mol/einstein) [a] x10^{-3}	K $_{OH•}$(M^{-1} S^{-1}) [a] x10^9	Predicted degradation (%)[a]	Contribution of photolysis (%) [a]	Degradation in this thesis (%)	
						Water	Urine
Amoxicillin	1.2	37.2	5.43	71	32	100	79
Caffeine	3.92	0.18	6.4	53	1	100	<1
Carbamazepine	6.07	0.06	8.02	61	1	100	48
Chloramphenicol	4.33	8.4	5.8	75	51	100	96
Ciprofloxacin	17.2	1.18	5.94	66	33	99	61
Diclofenac	4.77	29.2	8.38	97	92	100	97
HCTZ	6.65	4.1	5.7	70	41	100	96
Iopromide	21.0	3.9	3.3	86	80	100	100
Mefenamic acid	N/A	4.63	N/A	73	4	99	<1
Metoprolol	0.565	3.47	7.84	59	4	100	11
Metronidazole	2.1	0.34	17.9	88	1	100	98
Primidone	0.22	0.82	6.7	55	3	100	26
Sulfamethoxazole	13.2	3.79	5.82	80	62	100	97
Trimethoprim	2.94	0.118	6.3	52	1	100	<1

[a]Values from (Wols *et al.*, 2014). N/A- values are not reported.

Since urine contains OH•-scavenging organic matter, the less efficient oxidisers NO_3• and CO_3• are formed by UV treatment and these radicals react with organic matter, which compensates slightly for the scavenging effect of urine (Duca *et al.*, 2017; Pignatello *et al.*, 2006). These radicals can also inactivate urease enzyme by reacting with amino acid residues of cysteine and tryptophan, with a rate constant of 4.6×10^7 and 7×10^8 L mol^{-1} s^{-1}, respectively, at pH 7 (Neta *et al.*, 1988).

6.4. Enhancing degradation of OMPs and inactivation of enzymes

During UV-treatment of OMPs in water, all measured OMPs were degraded by more than 99%, whereas in real urine some compounds showed persistence during the treatment. Since the OMPs were degraded in water, there were obviously some constituents of urine which interfered with OMP degradation.

According to Clauß *et al.* (2008), UV lamps that can emit at lower wavelength (222 nm) result in faster inactivation of urease. In this thesis, it was observed that OMPs were degraded with a higher rate constant than in studies employing a UV lamp emitting only at 254 nm (Wols *et al.*, 2013; Zhang *et al.*, 2015). Therefore, use of UV lamps which deliver high fluence may result in high degradation. Degradation of OMPs and inactivation of urease could be further enhanced by increasing the transmittance of real urine through addition of oxidisers such as H_2O_2 (Wang *et al.*, 2018), $Na_2SO_2O_8$ (Zhang *et al.*, 2016a), ozone (Epold *et al.*, 2012) and Fenton (Pignatello *et al.*, 2006), which not only remove organic matter but also enhance formation of radicals like OH•, thereby increasing total degradation.

6.5. Implementation potential and challenges

6.5.1. Implementation potential

The results in this thesis show that it is possible to inactivate urease enzyme and remove OMPs present (spiked) in urine using UV treatment. Degradation of OMPs in urine required >10-fold more energy than degradation of OMPs in water, whereas inactivation of urease in urine required >21-fold and 52-fold more energy than inactivation of urease in

water and synthetic urine (without urea), respectively. Based on the volume of urine treated in this thesis, around 67 kWh of energy will be required to treat 1 m^3 of urine to achieve >50% degradation of OMPs and >99% inactivation of urease. Köhler *et al.* (2012) investigated removal of 14 OMPs from wastewater using a dichromatic low-pressure mercury UV lamp, and achieved overall 65% degradation of OMPs with an energy input of 6 kWh per m^3 of wastewater treated. Thus, close to 10-fold more energy is required to remove OMPs in urine. However, it should be noted that the volume of urine to be treated is much smaller, constituting 1% of total wastewater volume.

On average, an individual excretes 1.5 L of urine per day (Vinnerås *et al.*, 2006), and the average number of individuals per household is 2.3 in the European Union and 2.12 in Sweden (Savvidou *et al.*, 2020). Thus, on average 220 Wh of energy per day is required to treat urine from a single Swedish household, which is equivalent to using one 15-W lamp for around 14 hours or to 27% of the energy required by a refrigerator (790 Wh d^{-1}) (Sidler *et al.*, 2002). In Sweden, on average 9000 kWh y^{-1} dw^{-1} was consumed in 2019 (ODYSSEE-MURE, 2023) and 4400 kWh $person^{-1}$ in 2021 (Eurostat, 2023). Thus UV treatment of urine from one toilet would only add 0.86% to the total electricity demand of a Swedish household.

Furthermore, UV treatment as a pre-treatment to nutrient recovery by dehydration would only add 4% (234 MJ m^{-3} of urine) to the amount of energy estimated by Simha *et al.* (2020a) to be required to evaporate water from urine (5800 MJ m^{-3}). It should be noted that this energy demand could be reduced further by use of different kinds of UV lamps.

In Sweden, pharmaceutical sales represented an average defined daily dose of 1962 per 1000 inhabitants in 2022 (Swedish-eHealth-Authority, 2023). The units of defined daily dose differs from drug to drug and also for the same drug based on route of administration, *e.g.* defined daily dose for ciprofloxacin is 1 g with an oral administration route and 0.8 g with a parenteral route of administration (WHO, 2023). Diuretics, lipid-lowering drugs, antibiotics, cardiovascular drugs and sex hormones are among the most prescribed and purchased drugs (Wettermark *et al.*, 2007). For cardiovascular drugs, for example, the defined daily dose ranges from 0.8

mg (salbutamol) to 2 g (metformin) (Naliganti *et al.*, 2019). A report released by Stockholm City Council classified metformin as a persistent compound (Council, 2014). Metformin has been detected in 15 wastewater treatment plants in Sweden, with a mean concentration of 19.6 µg L^{-1} in ingoing wastewater and with 50% of this concentration detected in the effluent (Golovko *et al.*, 2021).

The main route of elimination for metformin is urine and 90% (equivalent to 1.8 g) may appear in urine (Wishart *et al.*, 2006). In the OMP degradation study in Paper II, metformin was degraded by 36% ± 3% by UV irradiation for 80 min. Thus, almost three-fold more energy is required to remove metformin by more than 90%. It should be noted that the spiking concentration of OMPs used in Paper II was 60 µg L^{-1}, which is comparable to concentrations detected in influent to wastewater treatment plants in Australia (D Yang *et al.*, 2022). However, higher concentration of OMPs are expected in urine as it is flushed with less water than faeces. While lower concentrations of individual OMPs were used in Paper II, the total sum of concentrations of OMPs used was about 3 mg L^{-1}. Thus, considering UV treatment for a single household setting where one member takes a single drug, *e.g*. metformin, comparable or better degradation can be expected for the UV irradiation time (80 min) used in Paper II. However, higher UV irradiation might be required for households with higher consumption of drugs, *e.g*. paracetamol can be present in concentrations of several g L^{-1} when consumed according to recommended doses and elderly people consume on average more than five different drugs at a time (Wettermark *et al.*, 2007).

In order for the UV system to be effective in stabilisation of urine, the UV source must be placed as close as possible to the urine diversion system, to minimise urea hydrolysis in biofilms formed along the urine collection pipe (Figure 2). In addition, the receiving system (storage or nutrient concentration system) must be as sterile as possible to inhibit growth of urease-producing bacteria.

Badeti *et al.* (2021) studied the impact of source separation of urine and reported that with 90% urine diversion, 22% of the operating costs (energy requirement representing 55%) of conventional WWT plants could be saved, in addition to substantial reductions (98% N_2O and 25% CO_2) in greenhouse

gas emissions. Thus, use of UV treatment for source-separated urine can add to the advantages obtained simply by diverting urine.

6.5.2. Implementation challenges

The main challenge in integrating a UV system with a diverted urine collection tank is cleaning of the UV-reactor, to remove any build-up of thin layer of film that accumulates in the UV sleeve. This problem generally occurs during UV treatment for disinfection of wastewater (US-EPA, 1999). Thus, frequent cleaning is required in between batches of treatment, which is commonly done by washing with citric acid or with a solution of vinegar and sodium hydrogen sulphite (US-EPA, 1999).

Another challenge is to eliminate urease-producing microorganisms deriving from cross-contamination of urine with faeces, since these microorganisms have the potential to survive UV treatment (Manuscript in preparation) and achieve regrowth. To overcome this challenge, the system must involve other stabilisation methods, such as acidification (Ray *et al.*, 2018) or alkalisation (Randall *et al.*, 2016; Simha *et al.*, 2020c). Stabilisation of urea with UV and dosing with citric acid used for washing could be a win:win solution, but further research at pilot scale is needed to investigate its effectiveness.

Furthermore, most UV lamps have a lifetime ranging from 8000 to 2000 h, giving rise to concerns about toxic waste if a mercury lamp is used (Pelayo *et al.*, 2023). While this thesis investigated degradation of OMPs and inactivation of urease using low-pressure mercury lamps, the underlying mechanism for system effectiveness was UVC light and the inherent radicals formed during treatment, *i.e*. similar results could be expected with a safer type of UV lamp with similar photon emission, *e.g*. UV LED lamp.

The system tested removed more than half of the OMPs spiked in samples and thus has potential to reduce the micropollutant risk involved in using urine-derived fertiliser. However, further investigations on the toxicity and transformation products of OMPs are required to fully quantify the risk reduction of using UV treatment for degradation of OMPs. The challenge in removing OMPs using UV is that some OMPs are not degraded in real urine, *e.g*. atenelol, azithromycin, bisoprolol, carbamazepine and 10 other OMPs evaluated in Paper II. However, all of the OMPs investigated in Paper II

showed >99% degradation in water, indicating that the persistence of some in real urine to UV treatment might arise from the interaction of OMPs with other constituents of urine. For example, photo-susceptible functional groups of OMPs may attach to colloids or organic matter in urine, resulting in shielding of functional groups on OMPs. Addition of oxidisers is required to overcome this, which is easier for centralised systems than for individual household settings.

7. Conclusions

Results of the investigation of the inactivation of urease enzyme and degradation of OMPs by UV treatment of real fresh human urine with a 15W low-pressure mercury lamp (185 nm and 254 nm) led to the following conclusions:

- Inactivation and degradation rate constants for urease and for 75 OMPs in water and in synthetic and real urine were determined following UV treatment.
- Inactivation of urease (> 99%) and degradation of OMPs (55±36 %) in real urine was achieved with UV irradiation time of 71 min and 80 min, respectively.
- Inactivation of urease and degradation of OMPs in all experimental matrices (water, synthetic and real urine) likely occurred due to a combination of direct and indirect photolysis.
- A few compounds in real urine (16 out of 75 OMPs spiked in samples) showed persistence toward UV treatment. Photochemical and physicochemical properties could not explain the observed degradation of OMPS in urine.
- To reduce enzyme activity in real urine to below the detection limit, >52-fold more electrical energy is required compared with inactivation in synthetic urine (without urea), while 10-fold more energy is required to degrade 90% of OMPs spiked in real urine compared with water.
- The energy demand for degrading OMPs in urine is considerably higher than that for degrading OMPs in wastewater when calculated per volume treated. However, total energy demand is less, as urine represents less than 1% of wastewater volume.

- Inner shielding effects and scavenging of free radicals by urea and other organic compounds in urine are the likely reasons for retarded enzyme inactivation and slow degradation of OMPs in urine compared with water and synthetic urine.
- Overall, UV treatment shows promise as a urine-stabilising and OMP-degrading approach that can be integrated as a pre-treatment step in urine-concentrating technologies.

8. Future research

It is of interest to address the following research topics in order to obtain a holistic understanding of UV treatment as an alternative technology for urine stabilisation and OMP reduction:

- Degradation by products and toxicity of OMPs after UV treatment of urine. Previous studies have shown that formation of degradation by-products with higher toxicity than the parent compounds is possible in such systems.
- Potential of UV treatment in killing off antimicrobial-resistant bacteria and removing antimicrobial resistance genes in urine.
- Organic matter (COD) reduction technologies for efficient OMP reduction and enzyme inactivation.
- Influence of fluid dynamics on both photoinactivation and photodegradation of OMPs during large-scale UV treatment of urine.

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Popular science summary

Sanitation, i.e. management of human excreta, is one of the societal challenges which was included in millennium development agenda (1990-2015) and continued to sustainable development agenda (2015-2030). Though advancements were made in achieving SDG-6 goals, there is still a very large gap in the provision of adequate sanitation services especially in developing countries. At the same time, global food demand is increasing as a result of population increase, requiring increased food production with limited arable land necessitating use of fertilisers to increase crop yield. Human excreta, on the other hand, contains valuable nutrients that can be used as a fertilizer to plants (N, P and K). Furthermore, the removal of nutrients, particularly nitrogen, in wastewater treatment plants is costly and can cause harmful effects on receiving water bodies (e.g. eutrophication) if these nutrients are released without proper treatment.

In human excreta, most of N, P and K are found in urine. Thus source separation of urine and recovery of nutrients is among the sustainable approaches of excreta management. However, source-separation of urine in urban setting and its consequent application in agricultural land is hindered by the logistic challenge of transporting the urine. Therefore, concentrating the nutrients in urine is a must. Different technologies have been developed over the years to recover the nutrients from urine, and there are reports about success, which showcased the possibility of recovering the nutrients from urine in Sweden and Switzerland.

In an effort to implement the nutrients as a dry fertiliser, maximizing the nitrogen recovery in the form of urea-N is challenged by the presence of urease enzyme and/or urease-producing bacteria in source separation

systems. Currently, chemical addition (acid/base) is the common working mechanism to stabilise urea-N in urine. Parallelly, because of the presence of micropollutants such as pharmaceuticals in urine presents another challenge from the consumer perspective that might hinder the applicability of urine-derived fertiliser.

Therefore, this thesis presents UV treatment as an alternative nutrient stabilisation (urease inactivation) and pharmaceutical degradation technology from source-separated human urine. Based on the experimental protocols followed, it was possible to inactivate urease enzyme by >99% and remove >50% of pharmaceuticals from source-separated urine. Therefore UV treatment can be a solution to stabilize urea-N and reduce pharmaceuticals in source separated urine thereby minimizing the risk of using urine-derived fertiliser.

On average a single person excretes an average 1.5 L of urine per day and a single dwelling in Europe is inhabited by 2.3 person. Therefore, an average 1.3 m^3 of urine is produced per dwelling in a year. Thus implementation of such technology in single household toilet would require 67 kWh m^{-3} of electrical energy which is equivalent to 27% of the electrical demand for a refrigerator or 9% of the total electricity demand of a single dwelling.

Populärvetenskaplig sammanfattning

Sanitet är en av samhällets utmaningar som ingick i millenniemålen (1990-2015) och fortsatte på agendan för SDG (hållbara utvecklingsmålen) (2015-2030). Även om framsteg gjordes för att uppnå SDG mål 6, finns det fortfarande ett mycket stort glapp i tillgängligheten för sanitet, särskilt i utvecklingsländer. Parallellt ökar den globala efterfrågan på mat som ett resultat av befolkningsökningen, vilket kräver ökad livsmedelsproduktion med begränsad åkermark vilket kräver användning av konstgödsel för att öka skörden. Människans avföring, å andra sidan, innehåller värdefulla näringsämnen som kan användas som gödsel (N, P och K). Att inte hantera dessa näringsämnen belastar idag reningsverken och/eller de vattendrag som avloppet hamnar i. Därför är korrekt hantering av mänskligt avföring och återvinning av näringsämnen som att hoppa två hinder med ett hopp.

I mänsklig avföring finns huvuddelen av urinens N, P och K. Källsortering av urin och återvinning av näringsämnen är därför bland de hållbara metoderna för hantering av avföring. Emellertid hindras källsortering av urin i stadsmiljö och sedan användning på jordbruksmark av den logistiska utmaningen att transportera urinen. Därför är det ett måste att koncentrera näringsämnena i urinen. Olika tekniker har utvecklats under åren för att återvinna näringsämnena från urin, och det finns tekniker som utvecklats med möjligheten att återvinna näringsämnena från urin i Sverige och Schweiz.

I ett försök att kommersialisera näringsämnena som ett torrt gödningsmedel, utmanas kväveåtervinningen som urea-N av ureasenzym och/eller ureasproducerande bakterier som kan hittas i de källsorterande systemen. För närvarande är kemisk tillsats (syra/bas) den vanliga arbetsmekanismen för

att stabilisera urea-N i urin. Samtidigt utgör förekomsten av mikroföroreningar som läkemedel i urinen en annan utmaning ur konsumentperspektivet som kan hindra användbarheten av gödselmedel från urin.

Därför presenterar denna avhandling UV-behandling som en alternativ näringsstabilisering (ureasinaktivering) och nedbrytningsteknologi för orginaska mikroföroreningar i källsorterad humanurin. Baserat på de genomförda experimenten, var det möjligt att inaktivera ureasenzym med >99 % och avlägsna >50 % av läkemedlen från källsorterad urin. Därför kan UV-behandling vara en lösning för att stabilisera ureakväve och reducera läkemedel i källurin och därigenom minimera risken med att använda gödsel från urin.

I genomsnitt utsöndrar en person 1,5 liter urin per dag, i medelbostaden i Europa bor 2,3 personer. Då kan en produktion av 1,3 m^3 urin per bostad och år förväntas. Implementering av tekniken i hushållets toalett skulle kräva 67 kWh m^{-3} elektrisk energi, vilket motsvarar 27 % av elbehovet för ett kylskåp eller 9 % av det totala elbehovet för en enskild bostad.

Acknowledgements

This work was funded by the Swedish International Development Co-operation Agency through the Institute of Biotechnology, Addis Ababa University, Ethiopia, and the Swedish University of Agricultural Sciences, Sweden, within the sub-programme "Nutrient stabilization and safety to enhance food security in Ethiopia"). I would like thank the Swedish government for funding the project.

I'm very lucky and thankful to be supervised by Björn Vinnerås, Foon Yin Lai, Lutz Ahrens, Annika Nordin and Adey Desta, as they provided excellent support, guidance and discussions throughout the studies. I highly appreciate their support and I have learned a lot from each of them. I'm also very grateful to work with Prithvi Simha on both papers.

My thanks go to the management team for the SIDA project at the Institute of Biotechnology, Addis Ababa University, for their support throughout the project; Duren Mussabek for letting me use his experimental set-up, colleagues at ET for supporting the study by donating their urine; and Anuron, Anastasia, Karoline and intern students who visited our group for thier support in the lab work and making life enjoyable.

II

Water Research 242 (2023) 120221

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Degradation of 75 organic micropollutants in fresh human urine and water by UV advanced oxidation process

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ARTICLE INFO

Keywords:
Circular sanitation
Fertiliser
Nutrient recycling
Pharmaceuticals
Urine diversion
Wastewater treatment

ABSTRACT

In household wastewater, a large proportion of organic micropollutants (OMPs) load is attributed to human urine. OMPs could pose a risk to human and environmental health when urine collected in source-separating sanitation systems is recycled as crop fertiliser. This study evaluated degradation of 75 OMPs in human urine treated by a UV-based advanced oxidation process. Fresh urine and water samples were spiked with a broad range of OMPs and fed into a photoreactor equipped with a UV lamp (185 and 254 nm) that generated free radicals *in situ*. Degradation rate constant and the energy required to degrade 90% of all the OMPs in both matrices were determined. At a UV dose of 2060 J m^{-2}, average ΣOMP degradation of 99% (±4%) in water and 55% (±36%) in fresh urine was achieved. The energy demand for removal of OMPs in water was <1500 J m^{-2}, but for removal of OMPs in urine at least 10-fold more energy was needed. A combination of photolysis and photo-oxidation can explain the degradation of OMPs during UV treatment. Organic substances (*e.g.* urea, creatinine) likely inhibited degradation of OMPs in urine by competitively absorbing UV-light and scavenging free radicals. There was no reduction in the nitrogen content of urine during treatment. In summary, UV treatment can reduce the load of OMPs to urine recycling sanitation systems.

1. Introduction

Domestic wastewater is a valuable resource since it contains water, nutrients and energy that can be recovered (Vinnerås et al., 2006), but it also contains organic micropollutants (OMPs) such as pharmaceuticals, personal care products and hormones. These pollutants are potentially (semi-)persistent, bioaccumulative and toxic to aquatic organisms (Zenker et al., 2014).

Around 80% of the wastewater produced worldwide is discharged directly to the environment without any treatment (Connor et al., 2017). Even when wastewater is processed by a municipal treatment plant (WWTP), OMPs are typically not efficiently removed by conventional treatment processes. For instance, Golovko et al. (2021) analysed the fate of 164 OMPs at 15 WWTPs in Sweden and found that ΣOMP concentration declined on average by only 60% during wastewater treatment, while several OMPs, including metoprolol, carbamazepine, diclofenac and most antibiotics, were not removed at all during WWTP treatment. Around 103 OMPs were detected in sewage sludge and 122 OMPs were detected in recipient waters in that study, with the concentrations of OMPs being 50% higher in samples taken downstream compared with upstream of the WWTPs (Golovko et al. (2021). Following subsequent transport, OMPs end up in reservoirs where drinking water is sourced. In a study by Malnes et al. (2022), OMPs were detected in more than half of river water samples (n = 60) and lake water (n = 33) samples from three of Sweden's largest lakes, which are used as a drinking water source. That study estimated that several tons of OMPs are released to the lakes every year (Malnes et al. (2022). Tröger et al. (2021) found average removal of OMPs of around 65% for drinking water treatment plants in Europe and Asia.

An alternative approach to manage nutrients (nitrogen (N) and phosphorus (P)) and OMPs in wastewater is to target the upstream source, by source-separating wastewater into different fractions (urine, faeces, greywater) (Simha et al., 2020). One fraction that has received much research attention is human urine, because it contributes just 1%

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https://doi.org/10.1016/j.watres.2023.120221
Received 11 February 2023; Received in revised form 17 May 2023; Accepted 10 June 2023
Available online 14 June 2023

of the volume but 80% of the N and 50% of the P and potassium (K) load to WWTPs (Vinnerås et al., 2006). Human urine can be recycled back to farmland and used as a crop fertiliser (Heinonen-Tanski et al., 2007), but there are concerns about this practice since it is estimated that urine contributes ≈64% (±27%) of the pharmaceuticals in wastewater (Lienert et al., 2007). Thus closing the loop by using urine as a fertiliser may introduce a new pathway for OMPs to circulate, posing a risk to human health and the environment (Larsen et al., 2021; Simha et al., 2018). Several attempts have been made to develop treatment techniques for removing or degrading OMPs in urine. For example, Pronk et al. (2006) achieved 92% removal of propranolol, ethinylestradiol, ibuprofen, diclofenac and carbamazepine from fresh urine by nanofiltration, but found that the treatment also removed phosphate and sulphate. Duygan et al. (2021) found that two months of storage was insufficient to degrade OMPs in hydrolysed urine, while biological nitrification efficiently degraded atazanavir, ritonavir and clarithromycin. Köpping et al. (2020) demonstrated that >90% of 11 OMPs could be removed from biologically nitrified and stored urine by adsorption onto activated carbon. Few other techniques to degrade pharmaceuticals in fresh human urine at source and at bathroom scale have been researched, but use of the ultraviolet (UV) radiation could be promising.

Treatment with UV radiation is widely applied for disinfection purposes in many drinking water treatment plants, but in advanced form it can also be used to degrade micropollutants through photolysis and photo-oxidation (Wols et al., 2013). Compared with conventional UV treatment, UV-based advanced oxidation involves addition of photocatalysts such as ozone, hydrogen peroxide (H_2O_2) and peroxydisulphate ($S_2O_8^{2-}$), which propagate a chain reaction involving free radicals and enhance the degradation of OMPs (Zhang et al., 2015). Free hydroxyl radicals can also be generated *in situ* during vacuum UV irradiation (VUV) (light wavelength <190 nm) (Krakkó et al., 2022; Zhang et al., 2015; Zoschke et al., 2014). Although many studies have evaluated use of UV-based advanced oxidation processes to degrade OMPs, they have limited the evaluation to treated water or mixed wastewater samples (Giri et al., 2015). Therefore, this study fills this gap by evaluating the degradation of OMPs in freshly excreted urine. Furthermore, our study provides knowledge on the degradation of micropollutants that was not reported previously (*e.g.* carazolol, budenoside, cetirizine, fexofenadine, encazamene, mirtazapine, oxycodone, pyrimethamine, simvastatin and sulindac).

The aim of this study was to evaluate degradation of OMPs in fresh source-separated human urine during UV treatment. Specific objectives were to: (i) determine the degradation behaviour and degradation rate constants for 75 OMPs in batch UV treatments of water and fresh human urine; (ii) estimate the UV dose required to degrade 90% of each OMP in water and fresh urine; and (iii) analyse the influence of the matrix (water *vs.* fresh urine) and the photochemical properties of the OMPs on their degradation during UV treatment.

2. Materials and method

2.1. Urine collection

Fresh urine donations ($n = 27$) were collected from volunteers (male and female, aged 20–65 years) one day before the experiment, using high-density polyethylene (HDPE) bottles with plug cap and lid, and refrigerated at 4 °C. Prior to use, the urine donations were pooled, mixed and allowed to reach room temperature (20 ± 2 °C).

2.2. Organic micropollutants

A total of 75 OMPs were analysed, including antibiotics, antidepressants, antihypertensives, non-steroidal anti-inflammatory drugs (NSAIDs), beta-blockers, anti-epileptics, antifungals, antihistamines, opioids and opiates, anthelminthics, anaesthetics, antidiabetics, sedatives, medications for treating cancer and Alzheimer's disease, an antilipidaemic, an antiplatelet, an antineoplastic and an antipsychotic, and personal care products, stimulants, vitamins, X-ray contrast agents, diuretics, a laxative, a diagnostic agent and an insect repellent (see Table S1 in Supplementary Information (SI)). A full list of the OMPs analysed, including their CAS registry number and photochemical properties (*i.e.* molar absorption coefficient (ε), quantum yield (Φ), and rate constant of hydroxyl radical (K_{OH^*}) is provided in Table S2 in SI. The 75 OMPs were selected based on environmental relevance (Howard et al., 2011), previous studies (Lienert et al., 2007; Wols et al., 2013; Yu et al., 2019) availability of analytical standards and analytical performance of the substances.

2.3. Photoreactor set-up

The study was carried out in a cylindrical photoreactor that consisted of the UV lamp surrounded by a quartz sleeve. A 15 W tubular low pressure (LP) mercury lamp (Heraeus, Hanau, Germany) with a fluence rate of 43 μW cm^{-2} as the UV light source was used in the experiments. According to the manufacturer (Heraeus, 2022), emission of light by the lamp at a relative output at 185 nm is an estimated 8% of the output at 254 nm. The lamp was fitted with a quartz sleeve and placed in a cylindrical reactor chamber with dimensions, 40 cm length and 3.7 cm diameter with a total volume of 430 mL. The reactor was connected to a peristaltic pump (Masterflex, Fisher Scientific, USA) using UV-resistant Tygon® tubing (internal diameter 4.8 mm). The pump circulated urine within the photoreactor at a rate of 40 mL min^{-1}. Samples of the treated urine were collected via a shut-off valve at the bottom of the column.

2.4. Degradation experiments

Two sets of experiments were performed, in which degradation of OMPs was evaluated in triplicate in spiked fresh human urine and Milli-Q water. Before each experiment, the UV lamp was switched on and operated for 10 min to ensure constant light emission. Then 300 mL of fresh urine or Milli-Q water were spiked with a standard solution (1800 μL of 10 ng $μL^{-1}$) containing a mixture of 75 OMPs (see Section 2.2), and thoroughly mixed over a magnetic stirrer for 5 min. This represented a concentration of 60 μg L^{-1} (*i.e.* 0.076 to 0.465 μM or 18 μg absolute mass) for each OMP, with an estimated total organic carbon (TOC) of 6 mg L^{-1} added becasue of spiking which is less than 5% of the TOC concentration (4 g L^{-1}) in fresh urine. A 15 mL sample of the spiked solution (time zero min) was sampled, while the rest was added to the photoreactor and the peristaltic pump was switched on. The photoreactor was operated for 80 min and 15 mL samples were collected after 1, 2.5, 5, 10, 20, 40 and 80 min of operation. When sampling, the first 2 mL were discarded as they were estimated to represent dead volume trapped in the valve. The 15 mL samples were divided into three equal portions by volume and transferred to 7 mL amber vials, among the three, 2 vials were used for analysis while the rest is kept as a backup. A mixture of mass-labelled chemicals (each 10 ng absolute mass; Table S3 in SI) as internal standards was added to two vials (each 5 mL). These samples were subjected to analyses of OMPs (Section 2.5) and other standard parameters (UV–vis, ammonium, chemical oxygen demand) (Section 2.6) (Figure S1 and Table S4 in SI).

Two control experiments were conducted in duplicate in dark conditions, where fresh urine and Milli-Q water spiked with OMPs were added to the photoreactor, but the UV lamp was not switched on. To block light irradiation, the reactor and the tubing were covered with aluminium foil. Samples were collected after 1, 10 and 80 min of residence time inside the reactor. As blank controls, in two duplicate experiments fresh urine and Milli-Q water without spiking with OMPs were added to the reactor and sampled only once, after 80 min of operation.

2.5. Extraction and analysis of OMPs

All urine and water samples were extracted using solid phase extraction (SPE) with Oasis HLB cartridges (6 mL, 150 mg sorbent, 60 μm). The cartridges were first conditioned with 5 mL methanol and 5 mL Milli-Q water, after which the samples (5 mL with internal standard chemicals, see Section 2.4) were loaded. The cartridges were then washed with 5 mL Milli-Q water, dried under vacuum for 30 min and eluted with 4 mL methanol. The eluted samples were concentrated to 200 μL extracts under a stream of nitrogen gas and reconstituted with 800 μL Milli-Q water to give a final volume of 1 mL.

Concentration of OMPs ($n = 75$) was analysed using a DIONEX UltiMate 3000 ultra-high pressure liquid chromatography system (Thermo Scientific, Waltham, MA, USA) coupled to a triple quadrupole mass spectrometer (TSQ QUANTIVA, Thermo Scientific, Waltham, MA, USA). Eight calibration standards in the range 0–400 ng mL^{-1} were analysed together with the samples. Chromatographic separation of OMPs was conducted using a Kinetex® biphenyl analytical column (100 × 2.1 mm, 2.6 μm) at 40 °C with a flow rate of 0.5 mL min^{-1} and mobile phases of Milli-Q water and methanol, each with 0.1% formic acid. The injection volume was 10 μL. Multiple reaction monitoring with two transitions for each chemical was used for data acquisition. This extraction and analytical methodology was also applied in previous studies by our research group (Golovko et al., 2021; Sörengård et al., 2019).

Over the eight-point calibration range, linearity of 0.9614–0.9998 was observed for the OMPs (Table S5 in SI). Limit of quantification (LOQ) ranged between 0.01 and 5.5 μg L^{-1} (0.03 to 40 nM) (Table S6 in SI). No contamination was observed during analysis of blanks with Milli-Q water in the same extraction batches, but sebacic acid, sertraline, caffeine, sulisobenzone, nicotine, methylparaben and budesonide were present in the fresh urine samples (Table S7 in SI). The initial concentration of sebacic acid and caffeine in urine was about 3-fold and 37-fold higher, respectively, than the concentration spiked in the sample. Average recovery of OMPs was 90±16% (Table S8 in SI).

2.6. Analysis of standard parameters

The pH was measured using an electrode (Fisher Scientific Accumet, 13–620-AE6, USA) attached to an Accumet AE150 pH metre (Fisher Scientific, USA). Electrical conductivity (EC) was measured using a probe (TetraCon 325, WTW, Germany) connected to a handheld EC metre (Cond 340i, WTW, Germany). UV absorbence measurements were made using a Lambda 365 UV–vis spectrophotometer (Perkin-Elmer, USA) within a scan window of 190–400 nm and a scanning rate of 480 nm min^{-1}. Urine samples were diluted 10-fold before the measurements, but Milli-Q water samples were not diluted.

To determine total solids (TS) content, 100 mL of fresh urine were dried in an oven at 105 °C for 24 h. To determine volatile solids (VS) content, the dried urine was combusted in a furnace (LH30/12, Nabertherm GmBH, Germany) at 650 °C for 6 h. A balance (Kern KB 2000–2NM, Germany; 0.01 g precision) was used to monitor the change in weight.

Concentrations of total nitrogen, total ammonium-nitrogen and chemical oxygen demand (COD) were analysed colorimetrically using Spectroquant® test kits (Merck KGaA, Darmstadt, Germany) and a photometer (NOVA 60 A, Merck KgaA, Germany). For measurements of COD and ammonium-nitrogen, urine was diluted 100-fold and analysed using, respectively, a Spectroquant® COD test kit (109,772) in the concentration range 10–150 mg L^{-1} and Spectroquant® ammonium test kit (100,683) in the concentration range 2–150 mg L^{-1}. For total nitrogen analysis, urine was diluted 1000-fold, digested using a Spectroquant® Crack-Set 20 test kit (114,963) and analysed for concentration of nitrate in the range 1–25 mg L^{-1} using a Spectroquant® nitrate test kit (109,713). The initial concentration of P, K, calcium (Ca) and magnesium (Mg) in fresh urine was determined by inductively coupled plasma-optical emission spectroscopy (Optima Avio 200, PerkinElmer, USA), prior to which samples were digested with 65% HNO_3 and diluted with Milli-Q water.

2.7. Kinetic modelling

Degradation (%) of OMPs was calculated as:

$$Degradation\ (\%) = \left(\frac{C_0 - C_t}{C_0}\right) \times 100 \quad (1)$$

where C_0 and C_t represent the concentration of OMPs initially (time zero min) and at the time of sampling, respectively.

The experimentally determined degradation of each OMP was plotted against treatment time and fitted to the pseudo first-order rate equation:

$$\ln\left(\frac{Ct}{C0}\right) = -kt \quad (2)$$

where t(min) is treatment time and k is the degradation rate constant (min^{-1}).

The time required to degrade the OMPs by 50% (t_{50}) (Eq. (3)) and 90% (t_{90}) (Eq. (4)) of their initial concentration was also calculated. The UV dose equivalent to the treatment time was calculated using the lamp fluence rate (Eq. (5)).

$$t_{50} = \frac{ln2}{k} \quad (3)$$

$$t_{90} = \frac{\ln(0.1)}{k} \quad (4)$$

$$UV\ dose\ \left(Jcm^{-2}\right) = fluence\ rate\ \left(Jcm^{-2}s^{-1}\right) * treatment\ time\ (s) \quad (5)$$

2.8. Statistical analysis

For the OMPs with concentrations below LOQ, half the LOQ value was used in statistical analysis of the data. The data on degradation of OMPs were tested for normality and homogeneity of variance. Analysis of variance (ANOVA) at 95% confidence interval was performed to compare degradation of the OMPs in water and in urine at different treatment times, with and without UV treatment. The degradation efficiency values were normalised so that the initial concentration difference in OMPs was not reflected in the variance. Major functional groups for OMPs studied were compiled using an online platform and the presence and absence of these functional groups were artificially coded to a dichotomous variables (zero and one) during analysis (Kentucky, 2023). Principal component analysis (PCA) was conducted using R software to evaluate whether predictor variables (functional groups properties of OMPs) could explain the variance in degradation of the OMPs in fresh urine due to UV treatment. Additionally, Point-biserial correlation was conducted using R software find significant correlation between functional groups and photocehmical properties with degradation of OMPs in urine. Linear regression analysis at 95% confidence interval was performed on the variables of interest. In the PCA and correlation analysis, the data for all OMPs were analysed together and as subsets for different therapeutic groups.

3. Results

3.1. Degradation of OMPs without UV treatment

In the dark controls (*i.e.* no UV irradiation) for water, after 80 min of treatment there was <20% degradation for 56 out of 75 OMPs, of which 47 OMPs exhibited <10% degradation, while there was <5% degradation for 39 OMPs. There was >90% degradation for atorvastatin, clopidogrel, encazamene, tamoxifen and simvastatin, while the degradation for ioperamide, meclofenamic acid, mefenamic acid and

valsartan varied between 50 and 70% (Figure S2A in SI).

In the dark controls for urine, after 80 min of treatment there was <20% degradation for 63 out of 75 OMPs, of which 52 OMPs exhibited <10% degradation. There was <5% degradation of 39 OMPs, including atenolol, azithromycin, carbamazepine and metformin. Clopidogrel, encazamene and tamoxifen were the only OMPs which exhibited >90% degradation (Figure S2B in SI).

3.2. Degradation of OMPs with UV treatment

In experiments treating water spiked with OMPs in the photoreactor with UV, >90% degradation of almost all OMPs (n = 73 of 75) was observed after 80 min of UV treatment (2100 J m^{-2}). The remaining two OMPs, memantine and sebacic acid, exhibited 71% and 83% degradation, respectively (Fig. 1).

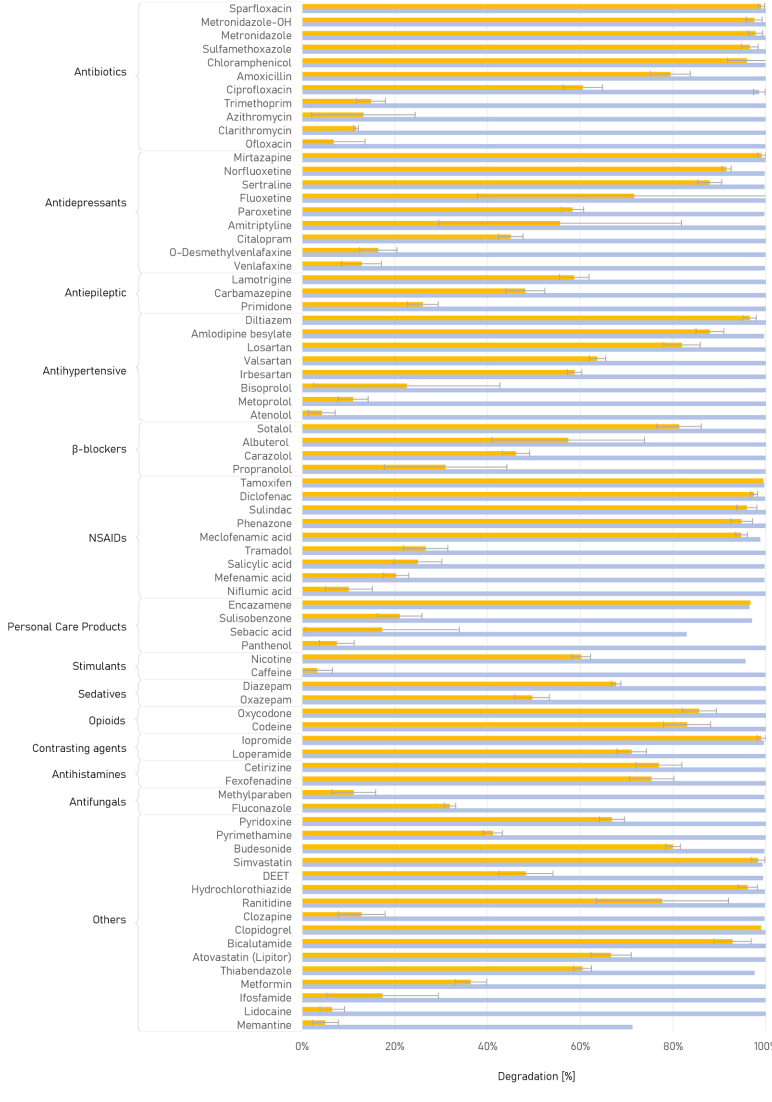

Fig. 1. Degradation (%) of 75 target OMPs after 80 min of UV treatment (UV dose 2060 J m^{-2}) of water (blue) and fresh urine (yellow). Average values are shown, error bars indicate standard deviation (n = 3). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

When fresh urine spiked with OMPs was treated with UV, >90% degradation was observed for 19 out of 75 OMPs after 80 min of treatment. The degradation varied from <1% (±0%) (azithromycin) to >99% (±1.0%) (chloramphenicol) for antibiotics, <1% (±0%) (atenolol) to 97% (±1.0%) (diltiazem) for antihypertensives, <13% (±4%) (venlafaxine) to 99% (±1%) (mirtazapine) for antidepressants, <1% (±0%) (niflumic acid) to 97% (±1%) (diclofenac) for NSAIDs, 26% (±3%) (primidone) to 59% (±4) (lamotrigine) for antiepileptics, 31% (±13%) (propranolol) to 81% (±5%) (sotalol) for β-blockers, and 1% (±0%) (sebacic acid) to 99% (±5%) (encazamene) for personal care products (Fig. 1). There was <1% degradation of atenolol, azithromycin, bisoprolol, caffeine, clozapine, ifosfamide, lidocaine, memantine, mefenamic acid, niflumic acid, ofloxacin, sebacic acid, sulisobenzone and trimethoprim (Fig. 1).

The average ΣOMP degradation during UV treatment was 99% (±4%, standard deviation) in water, which was significantly higher than the average degradation in urine (55% ±36%) ($p<0.0001$, $n = 75$). In comparison to the dark controls, UV treatment significantly enhanced the degradation of OMPs in both water and urine ($p<0.0001$, $n = 75$).

For some OMPs, degradation was highly variable (standard deviation >20%). These OMPs included metformin and cetirizine in the dark control for water, metformin and diclofenac in the dark control for urine, and fluoxetine, amitriptyline, albuterol, ranitidine and propranolol in UV-treated urine. Thus the results on degradation of these OMPs should be interpreted with caution. Apart from these compounds, the variability in degradation of OMPs during UV treatment was low (average standard deviation 6% in water and <5% in urine).

3.3. Degradation trends and kinetics

To illustrate the major trends observed in the experiments, degradation of four representative OMPs (clopidogrel, memantine, sulphamethoxazole, venlafaxine) was plotted against time for water and urine, with and without UV treatment (Fig. 2).

Clopidogrel was among the OMPs that was degraded in the dark controls. Tamoxifen and encazamene showed similar degradation behaviour to clopidogrel, with >90% degradation after 80 min in the dark control of both water and urine (Figures S1A and S1B in SI). Degradation of memantine in the dark controls (<5% after 80 min) was similar to that of 47 OMPs in water and 52 OMPs in urine (Figures S2A and S2B in SI).

During UV treatment of water, 18 OMPs showed >99% degradation after 1 min of treatment, which was similar to degradation of sulphamethoxazole (Fig. 3B). The half-life of 73 OMPs was less than 20 min (at ≈500 J m^{-2}) in water, with average OMP degradation of 75% (±30%), 82% (±27%) and 93% (±17%) after 1, 2.5 and 5 min of UV treatment, respectively (Table S9 in SI).

During UV treatment of urine, most OMPs showed degradation behaviour in between that of clopidogrel and venlafaxine (Figs. 2C and 2D). Of the 75 OMPs analysed, 18 OMPs had half-life of <20 min (≈500 mJ m^{-2}). The average degradation of OMPs was <15% (±15%), <30% (±24%) and 55% (±36%) after 5, 20 and 80 min of UV treatment, respectively (Table S9). The different starting concentrations for sulfamethoxazole and clopidogrel can be explained by degradation of the compounds and sorption effects before starting the experiment.

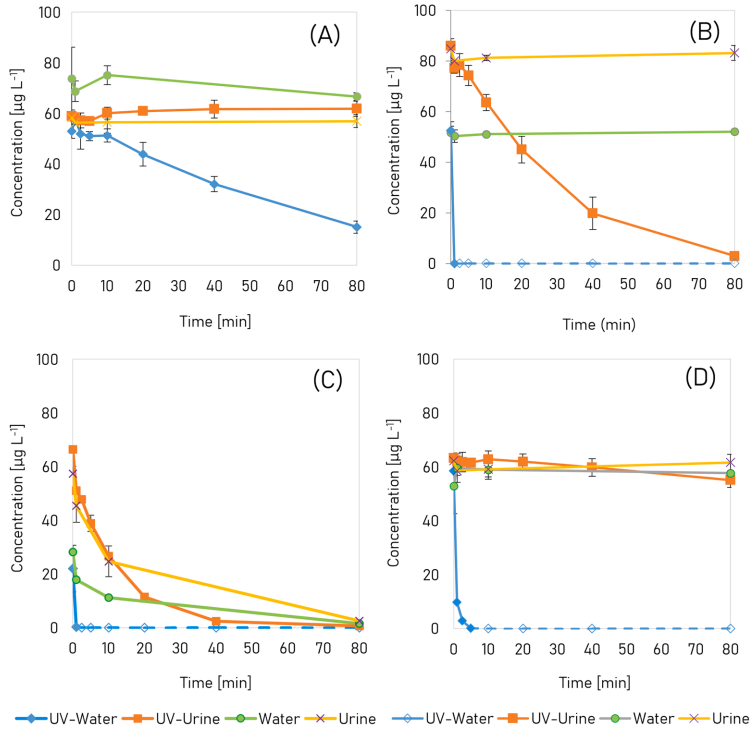

Fig.. 2. Degradation kinetics of (A) memantine, (B) sulfamethoxazole, (C) clopidogrel and (D) venlafaxine in water and fresh urine, with and without UV treatment. The open diamonds in B, C and D represent detection of the OMPs below their LOQ.

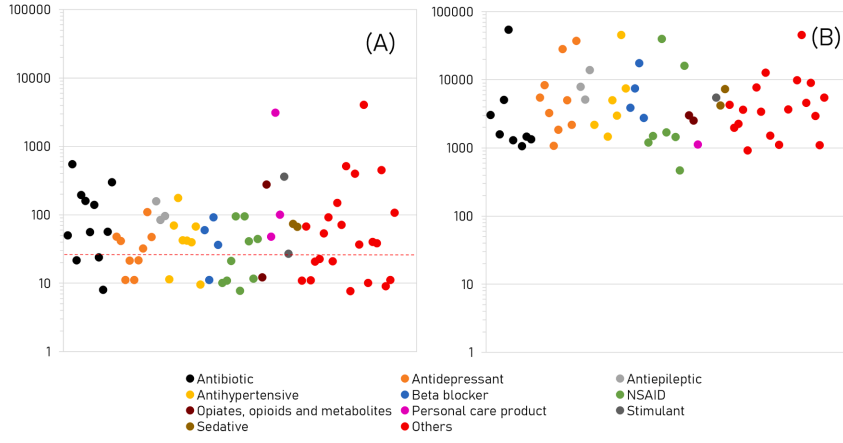

Fig. 3. Ultraviolet (UV) dose required to degrade 90% (UVe_{90}, J m^{-2}) of the 75 target OMPs in (A) water and (B) fresh urine. The y-axis shows UVe_{90} on a $\log_{10}$ scale and the x-axis a list of OMPs, arranged alphabetically. OMPs below the red dotted line have conservative E_{90} values as the concentration fell below LOQ within 1 min of UV treatment (at 26 J m^{-2}). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

To estimate the amount of energy required to degrade the OMPs by more than 90%, t_{90} for each compound was calculated according to Eq. (4) and the value was used to calculate the equivalent energy according to Eq. (5). To degrade the OMPs to more than 90% of their initial concentration in water, a UV dose of <1000 J m^{-2} was required, except for memantine and sebacic acid. Hydrochlorothiazide, a diuretic pharmaceutical, was not included in the energy demand calculations, as its degradation in UV-treated water could not be explained by pseudo first-order kinetics. In comparison, the UV dose required to degrade the OMPs to 90% of their initial concentration in urine was at least 10-fold higher and varied between 1000 and 20,000 J m^{-2} for most OMPs (Fig. 3). The exceptions, with even higher UV dose requirement, were clarithromycin, metoprolol, methylparaben, niflumic acid, *O*-desmethylvenlafaxine and venlafaxine (Table S9). The UV dose required for degrading 14 other OMPs in urine could not be estimated, as they were not degraded (highly persistent) during the treatment (Table S10 in SI). Since any loss of energy in the system was not considered, the energy requirement shown is an estimate based on the treatment time to degrade the OMPs, and actual energy requirement might differ in other set-ups or settings.

4. Discussion

This study evaluated degradation of 75 OMPs in water and fresh human urine during UV treatment. With UV treatment for up to 80 min (at 2100 J m^{-2}), more than 99% and 55% degradation of OMPs was observed in water and urine, respectively. However, degradation of OMPs in urine required 10-fold higher treatment time/energy input than degradation in water. In a previous study, Wols et al. (2013) reported >90% degradation of atenelol, proranolol, carbamazepine, sulfamethoxazole, venlafaxine, sotalol, fluoxetine and diclofenac following treatment with 5 mg L^{-1} H_2O_2 and a UV dose of 2000 J m^{-2} generated with a 60 W monochromatic (254 nm) LP lamp.

During UV treatment, OMPs can be degraded due to photolysis, photo-oxidation or a combination of both (Zhang et al., 2016). The type of UV lamp (185 nm and 254 nm) used in this study could generate hydroxyl free radicals in the treatment solution (Gonçalves et al., 2021). Therefore, degradation of OMPs during UV treatment was due to a combination of photolysis and photo-oxidation occurring simultaneously in the photoreactor.

The OMPs evaluated in this study absorbed light predominantly within the range 190–300 nm (Figure S1A in SI). According to Hokanson et al. (2016), OMPs with larger photolysis/molar absorption coefficient (ε) are more susceptible to UV photolysis. Since UV radiation at 185 nm and 254 nm was used in the present study, photodegradation of OMPs by direct photolysis likely occurred. For instance, high overall degradation rate constants in water were observed for photo-susceptible OMPs such as diclofenac (>5.9 min^{-1}), iopromide (>7.73 min^{-1}) and sulfamethoxazole (> 7.39 min^{-1}), presumably due to their high molar absorption coefficient (ε_{254} 6–23× 10^3 M^{-1} cm^{-1}) and high quantum yield (Φ_{254} 2.8–22 × 10^{-2} mol^{-1} E^{-1}) (Yu et al., 2019). Our results for the degradation rate constants are comparable to that of Kim et al. (2009) for carbamazepine (0.36 min^{-1}), diclofenac (1.8 min^{-1}), metoprolol (0.42 min^{-1}) and propranolol (0.3min^{-1}), even though they used an 8 W LP monochromatic UV lamp and 6 mg L^{-1} H_2O_2. This is because we used a UV lamp that emitted light at 185 nm, which allowed fast degradation without the addition of H_2O_2. For example, the degradation rate constant of venlafaxine in our study was 1.25 min^{-1}, whereas the degradation rate constant of venlafaxine was only 0.37 min^{-1} in a study by Giannakis et al. (2017) despite the addition of 100 mg L^{-1} of H_2O_2 during UV treatment using a 11 W LP lamp. Kim et al. (2015) have also observed a higher degradation rate constant for trimethoprim when using a UV lamp emitting at 185 nm and 254 nm (0.013 min^{-1}) compared to a monochromatic LP UV lamp emitting light only at 254 nm (0.0017 min^{-1}). In contrast, caffeine is photoresistant even though it absorbs photons (ε_{254} 4.2 × 10^3 M^{-1} cm^{-1}), and its quantum yield ($\Phi\varepsilon_{254}$ 0.003 mol^{-1} E^{-1}) is around 100-fold lower than that of diclofenac (Yu et al., 2019). Therefore, the degradation rate constant for caffeine (0.16 min^{-1}) was among the lowest observed in our study (Table S10 in SI).

In addition to photolysis, OMPs can be degraded by photo-oxidation by free radicals (Vogna et al., 2004). During vacuum UV irradiation, hydroxyl radicals (OH*) can be generated due to: i) homolysis and photochemical ionisation of water and ii) decomposition of ozone generated photochemically from oxygen in the gas phase (Zoschke et al., 2014). The reaction rate constants for photo-resistant OMPs such as caffeine, carbamazepine, atenolol, propranolol, primidone and trimethoprim with hydroxyl radicals are high (10–28 × 10^9 M^{-1} s^{-1}), in contrast to that of photo-susceptible OMPs such as iopromide (3 × 10^9 M^{-1} s^{-1}) (Yu et al., 2019). Degradation of the photo-resistant OMPs (caffeine, carbamazepine, atenolol, propranolol, primidone and

trimethoprim) in water (>99%) during UV treatment was dominated by photo-oxidation, since their reaction rate constant with OH* was high. Kim et al. (2009) investigated the contribution of direct and indirect oxidation to degradation of pharmaceuticals during UV treatment and found that indirect oxidation was responsible for up to 90% of the degradation for photoresistant compounds such as DEET, carbamazepine and metoprolol.

Unlike water, fresh urine is a complex solution. The urine used in the present study had an organic matter content of 10 g COD L^{-1} (Table S4 in SI). Urine can contain hundreds of organic substances and metabolic breakdown products (Bouatra et al. (2013) and some of these organic substances, such as creatinine and amino acids, have high UV absorbence (Yokoyama et al., 2005). The major organic compound in urine is urea, which absorbs UV light between 190 nm and 220 nm. The concentration of urea measured in the fresh urine used in this study was 4.5 g L^{-1}, which is 750-fold higher than the concentration of ΣOMP added to the urine at the start of the treatment (Table S4 in SI).

Organic and inorganic substances in urine can influence UV oxidation of OMPs in several ways. First, they can competitively absorb incident photon flux (inner filter effect) (Doll et al., 2003) and reduce the degradation of OMPs due to direct photolysis (*e.g.* urea and creatinine) (Figure S1B in SI). Second, they can scavenge reactive species and free radicals like OH* and O_3, and thus reduce the photo-oxidative degradation rate of OMPs. Third, hydroxyl radicals can react with organic compounds in urine to form intermediate radicals that propagate the advanced oxidation process (Pignatello et al., 2006).

Two of the major scavengers in fresh urine are urea and ammonia (Giannakis et al., 2018; Zhang et al., 2015). After 80 min of UV treatment, there was no change in total nitrogen concentration in the urine samples in this study, but the concentration of urea decreased by 18% and the concentration of ammonium decreased by 20% (Table S4 in SI). Long et al. (2019) reported comparable urea photooxidation (22%) during 2 h treatment in swimming pool water using a low pressure UV lamp emiting at both 185 and 254 nm. Furthermore, Yang et al. (Yang, 1998) reported photooxidation of ammonia to nitrate and nitrite. In the present study, we observed a 46% increase in nitrate-nitrogen, but this increase did not correspond directly to the decrease in both ammonia-nitrogen or urea-nitrogen (Table S4).

After 80 min of UV treatment, the concentration of COD in urine decreased from 10 g L^{-1} to 8.2 g L^{-1}(19%), which is in line with the decrease in light absorbence at 254 nm (Figure S1B). COD is used as a surrogate for removal of organic pollutants in wastewater treatment (Altmann et al., 2014). A 20% reduction in COD was observed by Giannakis et al. (2017) after 4 h of UV treatment of real urine using a 35 W monochromatic (254 nm) UV lamp. In our study, average ΣOMP degradation in urine was only 55% (±36%) and some UV-resistant OMPs such as atenolol and caffeine could not be degraded by UV treatment (Table S9 in SI). For further degradation of ΣOMP, considerably higher energy input is required (Table S10 in SI), and could be supplied either by increasing the treatment time or by using higher wattage UV lamps (Wols et al., 2013). In addition, improved degradation of the OMPs in fresh urine could be achieved by supplementing the UV treatment with photocatalysts such as H_2O_2 (Wols et al., 2013), peroxydisulphate (Wang et al., 2020), titanium oxide and ozone (Vogna et al., 2004).

To predict the degradation of OMPs, principal component analyses were done to test the influence of presence or absence of major functional groups (arene, amine, benzene, etc.) of OMPs on their degradation in fresh urine. However, the presence or absence of these functional groups could only explain 14.19% (PC1) and 14.92% (PC2) of the degradation. Additionally, a significant correlation between functional groups of OMPs and their degradation could not be found, irrespective of whether the original dataset including all 75 OMPs was used or a subset of the data dividing the OMPs into different therapeutic groups was used (Table S11 and Table S12-A). Furthermore, OMPs degradation in urine was correlated against OMPs photochemical properties (molar absorption coefficient (ε), quantum yield (Φ) and rate constant for hydroxyl radical (K_{OH^*}), but no significant correlation could be found with either of the photochemical properties (Table S2 and Table S12-B). However, when we use the subset of OMPs (therapeutic groups), a strong positive correlation was observed between degradation of antihypertensives in urine with K_{OH^*}, ε and Φ, which suggests that these groups of OMPs can be degraded by both photolysis and photo-oxidation (Table S12-B). However, a strong positive correlation with Φ of beta-blockers and a negative correlation with K_{OH^*} points out that this group of OMPs are degraded by photolysis rather than photo-oxidation (Table S12-B).

Although no significant correlation ($p > 0.05$) could be found for all of the OMPs degradation with either of the photochemical properties or major functional groups, the OMPs could be degraded through the following major photodegradation routes suggested by Ahmad et al. (2016): (i) Photoaddition, (ii) Photoaquation, (iii) Photocyclization, (iv) Photodealkylation, (v) Photodecarboxylation, (vi) Photodehalogenation, (vii) Photodehydrogenation, (viii) Photodimerization, (ix) Photoelimination, (x) Photoinduced hydrolysis, (xi) Photoisomerization, (xii) Photooxidation, (xiii) Photoinduced rearrangement, (xiv) Photoreduction, and, (xv) Photoinduced ring cleavage.

Among the 75 OMPs evaluated in this study, information on degradation pathways is available for meclofenamic acid (photocyclisation), norfloxacin (photodehalogenation), (Ahmad et al., 2016), diclofenac (decarboxyllation), atenelol (hydroxylation) (Salgado et al., 2013), sulphamethoxazole (desulphonamidation, photoelimination, hydroxylation), amitryptiline (photohydration) (Nassar et al., 2017), tamoxifen (hydroxylation) (Ferrando-Climent et al., 2017), sertraline (dechlorination and dehydration) (Calza et al., 2021), salicyclic acid (hydroxylation) (Milovac et al., 2014), rantidine (denitration) (Dong et al., 2017), oxazepam (hydroxylation) (Kosjek et al., 2012), diazepam (hydroxylation and demethylation) (Mitsika et al., 2021), cetirizine (dechlorination and dehydroxylation) and fexofenadine (deamination and dehydroxylation) (Liu et al., 2022). Additionally, Lin et al. (2022) reported transformation pathways for antidepressants including citalopram, fluoxetine, sertraline and venlafaxine. For a full understanding of the effects of UV treatment prior to implementation, further evaluation of the photodegradation products and their degradation rate is required, since photodegradation products can have longer half-lives and can potentially be more toxic than the parent compounds (Voigt et al., 2017; Zhang et al., 2016).

5. Conclusions

Degradation behaviour and degradation rate constants were determined for 75 OMPs in water and fresh human urine during UV treatment using a dichromatic lamp (185 nm and 254 nm). A UV treatment duration of 1 min (26 J m^{-2}) gave ΣOMP degradation of 75% in water and 11% in urine. Increasing the UV treatment time to 80 min (2100 J m^{-2}) increased ΣOMP degradation to 99% in water and 55% in urine. The degradation rate constant of the OMPs ranged in value from 0.01 to 7.7 min^{-1} in water, whereas the maximum value observed in fresh urine was 0.13 min^{-1} (for tamoxifen). Compared with degradation of OMPs in water, the energy demand for degrading OMPs to <10% of their initial concentration in fresh urine was at least 10-fold higher. Of the 75 OMPs analysed, 16 OMPs were not degraded in urine by UV treatment. Scavenging of free radicals by urea and ammonia, combined with high initial organic matter content of urine (10 g COD L^{-1}), might be responsible for the slow degradation kinetics of OMPs in urine. However, the UV treatment resulted in no notable change in total nitrogen concentration, which is an advantage in the case of fresh urine intended for use as concentrated fertiliser. Overall, the results show that UV treatment can be a promising on-site process to reduce the load of OMPs to urine recycling sanitation systems.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

The study was supported by funding from Swedish International Development Co-operation Agency (through the Institute of Biotechnology, Addis Ababa University, Ethiopia and the Swedish University of Agricultural Sciences, Sweden, within the sub-programme "Nutrient stabilization and safety to enhance food security in Ethiopia"), and Stiftelsen Lantbruksforskning for the project "Micropollutant-free sustainable beer production" (Grant Number O-22-23-744). Colleagues at SLU are thanked for donating urine.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2023.120221.

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Supplementary information I

Photoinactivation of jack bean (Canavalia ensiformis) urease in fresh human urine using dichromatic low-pressure UV irradiation

Table S1. Composition of synthetic urine (based on a recipe taken from Ray *et al.* (2018))

Compound	**Concentration (g L^{-1})**
NaCl	2.5715
Na_2SO_4	2.1305
KCl	2.982
$MgCl_2.6H_2O$	0.813
NaH_2PO_4	2.3995
$CaCl_2.2H_2O$	0.588
Urea	10
pH	6

Table S2. Physicochemical properties and composition of real fresh urine

pH	6.94
EC	7.98 mS cm^{-1}
Total solids	0.58 g L^{-1}
Volatile solids	0.27 g L^{-1}
Total nitrogen	5.06 g L^{-1}
Total ammonia nitrogen, TAN	180 mg L^{-1}
Ca	0.03 g L^{-1}
K	0.87 g L^{-1}
Mg	0.03 g L^{-1}
Na	0.28 g L^{-1}
P	0.24 g L^{-1}
S	0.56 g L^{-1}

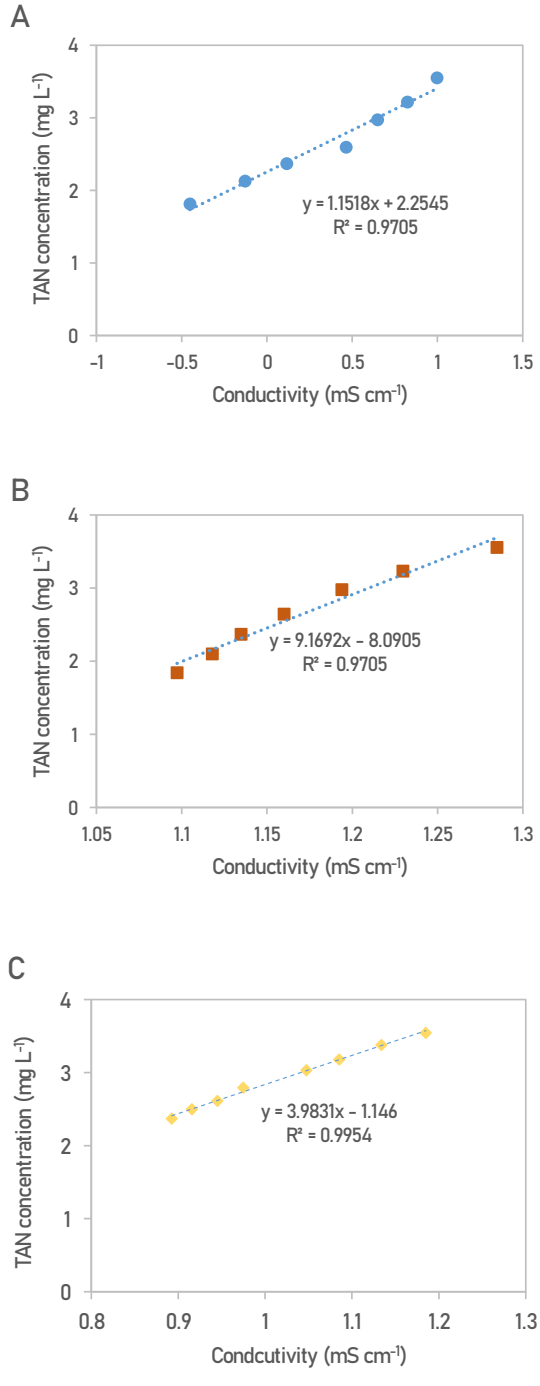


Fig. S1. Concentration of total ammonia nitrogen (TAN, mg L^{-1}) versus electrical conductivity (mS cm^{-1}) for urease-spiked (A) water containing urea, (B) synthetic fresh urine and (C) real fresh urine in absence of UV. TAN concentration and conductivity values are both log_{10}-transformed for regression analysis. Filled blue circles represent measured values and dashed line shows linear fit to experimental data.

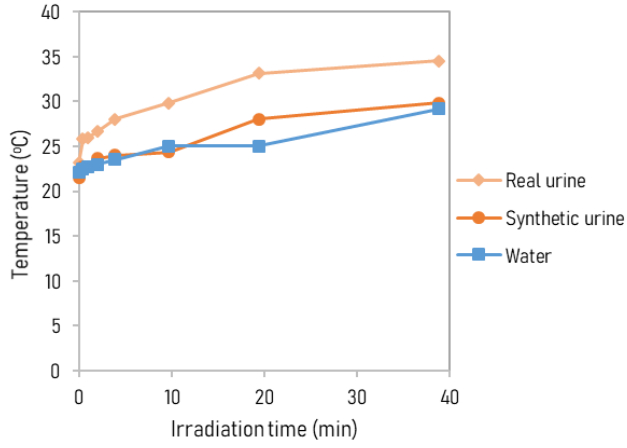


Fig. S2. Average temperature recorded for samples taken after exposure to different level of UV irradiance time for water, synthetic urine and real urine matrix.

Supplementary information II

Degradation of 75 organic micropollutants in fresh human urine and water by UV advanced oxidation process

Table S1. Target analytes (OMPs) in this study

1	Albuterol (Salbutamol)	26	Enzacamene	51	Ofloxacin
2	Amitriptyline	27	Fexofenadine	52	Oxazepam
3	Amlodipine besylate	28	Fluconazole	53	Oxycodone
4	Amoxicillin	29	Fluoxetine	54	Paroxetine
5	Atenolol	30	Hydrochlorothiazide	55	Phenazone
6	Atovastatin (Lipitor)	31	Ifosfamide	56	Primidone
7	Azithromycin	32	Iopromide	57	Propranolol
8	Bicalutamide	33	Irbesartan	58	Pyridoxine (Vitamin B6)
9	Bisoprolol	34	Lamotrigine	59	Pyrimethamine
10	Budesonide	35	Lidocaine	60	Ranitidine
11	Caffeine	36	Loperamide	61	Salicylic acid
12	Carazolol	37	Losartan	62	Sebacic acid
13	Carbamazepine	38	Meclofenamic acid	63	Sertraline
14	Cetirizine	39	Mefenamic acid	64	Simvastatin
15	Chloramphenicol	40	Memantine	65	Sotalol
16	Ciprofloxacin	41	Metformin	66	Sparfloxacin
17	Citalopram	42	Methylparaben	67	Sulfamethoxazole
18	Clarithromycin	43	Metoprolol	68	Sulindac
19	Clopidogrel	44	Metronidazole	69	Sulisobenzone
20	Clozapine	45	Metronidazole-OH	70	Tamoxifen
21	Codeine	46	Mirtazapine	71	Thiabendazole
22	DEET	47	Nicotine	72	Tramadol
23	Diazepam	48	Niflumic acid	73	Trimethoprim
24	Diclofenac	49	Norfluoxetine	74	Valsartan
25	Diltiazem	50	O-Desmethylvenlafaxine	75	Venlafaxine

Table S2-A. Physico-chemical properties of the 75 OMPs investigated in this study

Category	Compound	CAS number	Molecular formula	MW (g mol^{-1})	Log K_{ow}[a]	Water solubility at 25 ^{O}C (mg L^{-1})[b]	pK_a[c]	Main elimination route[d]	% excretion[e]
Beta blocker	Albuterol (Salbutamol)	18559-94-9	C13H21NO3	428	5	0	4	Urine	58-78% (60% unchanged)
Antidepressant	Amitriptyline	50-48-6	C20H23N	256	3	140	6	Urine	25-50% (2% unchanged)
Antihypertensive	Amlodipine besylate	88150-42-9	C20H25ClN2O5 · C6H5SO3H	234	2	4100	8	Urine	10% unchanged
Antibiotic	Amoxicillin	1026787-78-0	C16H19N3O5S	477	5	0	14	Urine	70-80%
Antihypertensive	Atenolol	29122-68-7	C14H22N2O3	422	4	0	4	Urine	85%
Antilipidemic agents	Atorvastatin (Lipitor)	134523-00-5	C33H35FN2O5	295	6	30	4	Urine	1%
Antibiotic	Azithromycin	83905-01-5	C38H72N2O12	241	5	20	4	Urine	6% unchanged
Antineoplastic agent	Bicalutamide	90357-06-5	C18H14F4N2O4S	179	3	8	10	N/A	N/A
Antihypertensive	Bisoprolol	66722-44-9	C18H31NO4	129	-3	1000000	3	Urine	50%
Corticosteroid drug	Budesonide	51333-22-3	C25H34O6	152	2	2500	8	Urine	60% (all in metabolite form)
Stimulant	Caffeine	58-08-02	C8H10N4O2	267	2	16900	10	Urine	N/A
Beta blocker	Carazolol	57775-29-8	C18H22N2O2	171	0	9500	3	N/A	N/A
Antiepileptic	Carbamazepine	298-46-4	C15H12N2O	187	-1	166700		Urine	N/A
Antihistamine	Cetirizine	83881-51-0	C21H25ClN2O3	265	3	39	7	Urine	70-85%
Antibiotic	Chloramphenicol	56-75-7	C11H12Cl2N2O5	162	1	1000000	9	N/A	N/A
Antibiotic	Ciprofloxacin	85721-33-1	C17H18FN3O3	282	4	19	2	Faeces/urine	62% / 45% (27% unchanged)
Antidepressant	Citalopram	59729-33-8	C20H21FN2O	295	4	36	10	Urine	12-23% unchanged
Antibiotic	Clarithromycin	81103-11-9	C38H69NO13	263	3	3670	10	Urine	20-30%
Antiplatelet drug	Clopidogrel	113665-84-2	C16H16ClNO2S	361	0	10810	8	Urine	50%
Antipsychotic	Clozapine	5786-21-0	C18H19ClN4	287	2	20	2	Urine	50%

Category	Compound	CAS number	Molecular formula	MW (g mol^{-1})	Log K_{ow}[a]	Water solubility at 25 ^{O}C (mg L^{-1})[b]	pK_a[c]	Main elimination route[d]	% excretion[e]
Opiates, opioids and metabolites	Codeine	76-57-3	C18H21NO3	315	1	4250	9	Urine	90% (10% unchanged)
Insect repellents	DEET	134-62-3	C12H17NO	329	4	35	10	Urine	50%
Sedative	Diazepam	439-14-5	C16H13ClN2O	188	0	100000	1	Urine	N/A
NSAID	Diclofenac	15307-86-5	C14H11Cl2NO2	218	1	500	12	Urine	70%
Antihypertensive	Diltiazem	42399-41-7	C22H26N2O4S	259	3	62	10	Urine	2-4% unchanged
Personal care product	Enzacamene	36861-47-9	C18H22O	169	1	78800	9	Faeces/urine	N/A
Antihistamine	Fexofenadine	83799-24-0	C32H39NO4	249	3	10	7	Faeces/urine	80% / 11 %
Antifungal	Fluconazole	86386-73-4	C13H12F2N6O	314	0	74530	8	Urine	80% unchanged & 11% as metabolites
Antidepressant	Fluoxetine	54910-89-3	C17H18F3NO	138	2	2240	3	Urine	N/A
Diuretic	Hydrochlorothiazide	58-93-5	C7H8ClN3O4S2	202	2	1000	5	Urine	N/A
Anticancer	Ifosfamide	3778-73-2	C7H15Cl2N2O2P	305	5	4	10	Urine	70-86% (61% unchanged)
Contrast agent	Iopromide	73334-07-3	C18H24I3N3O8	418	5	0	4	Urine	97%
Antihypertensive	Irbesartan	138402-11-6	C25H28N6O	272	0	16250	8	Faeces/urine	80% / 20%
Antiepileptic	Lamotrigine	84057-84-1	C9H7Cl2N5	392	0	8812	6	Urine	94% (46-87 % as metabolites)
Anesthetic	Lidocaine	137-58-6	C14H22N2O	253	1	379	2	Urine	5 % unchanged
Contrast agent	Loperamide	53179-11-6	C29H33ClN2O2	356	3	3000	4	Faeces	N/A
Antihypertensive	Losartan	114798-26-4	C22H23ClN6O	308	0	250000	-2	Faeces/urine	65% / 35% (6% unchanged)
NSAID	Meclofenamic acid	644-62-2	C14H11Cl2NO2	372	6	0	9	Urine/faeces	35% / 62%
NSAID	Mefenamic acid	61-68-7	C15H15NO2	201	2	50	10	Urine/faeces	20%
Alzheimer	Memantine	19982-08-2	C21H21N	263	3	1151	9	Urine	48% unchanged
Antidiabetic	Metformin	657-24-9	C4H11N5	290	1	400	7	Urine	90%

Category	Compound	CAS number	Molecular formula	MW (g mol^{-1})	Log K_{ow}[a]	Water solubility at 25 ^{O}C (mg L^{-1})[b]	pK_a[c]	Main elimination route[d]	% excretion[e]
Antifungal preservative	Methylparaben	99-76-3	C8H8O3	435	4	1	4	N/A	N/A
Antihypertensive	Metoprolol	37350-58-6	C15H25NO3	277	3	312	9	Urine	5% unchanged
Antibiotic	Metronidazole	443-48-1	C6H9N3O3	428	5	0	4	Urine	60-80%
Metabolite of antibiotic	Metronidazole-OH	4812-40-2	C6H9N3O4	256	3	140	6	N/A	N/A
Antidepressant	Mirtazapine	85650-52-8	C17H19N3	234	2	4100	8	Urine/Faeces	75% /15%
Stimulant	Nicotine	54-11-5	C10H14N2	477	5	0	14	Urine	10% unchanged
NSAID	Niflumic acid	4394-00-7	C13H9F3N2O2	422	4	0	4	N/A	N/A
Antidepressant	Norfluoxetine	56161-73-0	C16H16F3NO	295	6	30	4	N/A	N/A
Antidepressant	O-Desmethylvenlafaxine	93413-62-8	C16H25NO2	241	5	20	4	Urine	45% unchanged
Antibiotic	Ofloxacin	82419-36-1	C18H20FN3O4	179	3	8	10	Urine	65-80% unchanged
Sedative	Oxazepam	604-75-1	C15H11ClN2O2	129	-3	1000000	3	Urine	21% unchanged
Opiates, opioids and metabolites	Oxycodone	76-42-6	C18H21NO4	152	2	2500	8	Urine	74% (9% unchanged)
Antidepressant	Paroxetine	61869-08-7	C19H20FNO3	267	2	16900	10	Urine	64% (2% unchanged)
NSAID	Phenazone	60-80-0	C11H12N2O	171	0	9500	3	N/A	N/A
Antiepileptic	Primidone	125-33-7	C12H14N2O2	187	-1	166700		Urine	73-81 %
Beta blocker	Propranolol	525-66-6	C16H21NO2	265	3	39	7	Urine	91% (as metabolite form)
Vitamin	Pyridoxine (Vitamin B6)	65-23-6	C8H11NO3	162	1	1000000	9	Urine	N/A
Taxoplasmosis treatment	Pyrimethamine	58-14-0	C12H13ClN4	282	4	19	2	N/A	N/A
Antisecretory agent	Ranitidine	66357-35-5	C13H22N4O3S	295	4	36	10	Urine	30% unchanged
NSAID	Salicylic acid	69-72-7	C7H6O3	263	3	3670	10	N/A	N/A
Personal care product	Sebacic acid	111-20-6	C10H18O4	361	0	10810	8	N/A	N/A

Category	Compound	CAS number	Molecular formula	MW (g mol^{-1})	Log K_{ow}[a]	Water solubility at 25 ^{O}C (mg L^{-1})[b]	pK_a[c]	Main elimination route[d]	% excretion[e]
Antidepressant	Sertraline	79617-96-2	C17H17Cl2N	287	2	20	2	Urine	mostly metabolite
Statins	Simvastatin	79902-63-9	C25H38O5	315	1	4250	9	Faeces/urine	60% / 13%
Beta blocker	Sotalol	3930-20-9	C12H20N2O3S	329	4	35	10	Urine	80-90% unchanged
Antibiotic	Sparfloxacin	110871-86-8	C19H22F2N4O3	188	0	100000	1	N/A	N/A
Antibiotic	Sulfamethoxazole	723-46-6	C10H11N3O3S	218	1	500	12	Urine	85% (30% unchanged)
NSAID	Sulindac	38194-50-2	C20H17FO3S	259	3	62	10	Urine	N/A
Personal care product	Sulisobenzone	4065-45-6	C14H12O6S	169	1	78800	9	N/A	N/A
NSAID	Tamoxifen	10540-29-1	C26H29NO	249	3	10	7	Faeces/urine	27% / 25%
Antihelminthic	Thiabendazole	148-79-8	C10H7N3S	314	0	74530	8	Almost completely metabolised	
NSAID	Tramadol	27203-92-5	C16H25NO2	138	2	2240	3	Urine	90% (30% unchanged)
Antibiotic	Trimethoprim	738-70-5	C14H18N4O3	202	2	1000	5	Urine	50%-60% (80% unchanged)
Antihypertensive	Valsartan	137862-53-4	C24H29N5O3	305	5	4	10	Faeces/urine	83% / 13% (20% as metabolites)
Antidepressant	Venlafaxine	93413-69-5	C17H27NO2	418	5	0	4	Urine	87% (5% unchanged)

Remark

[a & b] - WSKOW v1.42 estimate, (EPI: Estimation Program Interface (EPI) Suite, from EPA US environmental protection agency); https://www.epa.gov/tsca-screening-tools

[c] - Physico chemical property of compounds; https://go.drugbank.com/

[d & e] - Elimination route option from the property option of compounds; https://go.drugbank.com/

Table S2-B. Photo-chemical properties for OMPs investigated in this study

Compound	K_{OH^*} (M^{-1} S^{-1}) x10^9	Reference	ε ($M^{-1}cm^{-1}$) x10^3 @ 254 nm	Φ (mol/einstein) x10^{-3}	pH	Reference
Albuterol (Salbutamol)	6	(Mathon *et al.*, 2021)	0	29	7	(Li *et al.*, 2022)
Amitriptyline	8	(Nassar *et al.*, 2017)	12.0	65	6.1	(Nassar *et al.*, 2017)
Amlodipine besylate	N/A		37.3	4	7	(Zhu *et al.*, 2015)
Amoxicillin	5	(Wols *et al.*, 2012)	1.20	372	7	(Wols *et al.*, 2012)
Atenolol	7	(Wols *et al.*, 2014)	0.35	65	6.4	(Wols *et al.*, 2014)
Atorvastatin (Lipitor)	19	(Zoumpouli *et al.*, 2020)	N/A	0.024	7	(Ping *et al.*, 2021)
Azithromycin	3	(Zoumpouli et al., 2020)	0.02	1220	7	(Voigt *et al.*, 2017)
Caffeine	6	(Wols *et al.*, 2012)	3.92	1.8	8	(Wols *et al.*, 2012)
Carbamazepine	8	(Wols *et al.*, 2012)	6.07	0.6	7	(Wols *et al.*, 2012)
Chloramphenicol	6	(Wols *et al.*, 2012)	4.33	84.0	7.5	(Wols *et al.*, 2012)
Ciprofloxacin	6	(Pereira *et al.*, 2007)	12.9	44.2	7	(Guo *et al.*, 2013)
Citalopram	N/A		N/A	0.26	9	(Kwon *et al.*, 2005)
Clarithromycin	4	(Mathon *et al.*, 2021)	N/A	N/A		
DEET	8		1.0	3.9	7.8	(Zhou *et al.*, 2020)
Diazepam	6	(You *et al.*, 2021)	16.4	2.0	7	(You *et al.*, 2021)
Diclofenac	8	(Wols *et al.*, 2012)	4.8	293.0	7	(Wols *et al.*, 2012)
Diltiazem	N/A		39.2	498	7	(Zhu *et al.*, 2015)
Fluconazole	4	(Lee *et al.*, 2014)	0.44	23	7	(Chen *et al.*, 2014)
Fluoxetine	9	(Wols *et al.*, 2014)	0.73	410	7	(Wols *et al.*, 2014)
Hydrochlorothiazide	6	(Wols *et al.*, 2012)	6.65	41	7	(Wols *et al.*, 2012)
Ifosfamide	4	(Wols *et al.*, 2013)	N/A	N/A		(Wols *et al.*, 2013)
Iopromide	3	(Wols *et al.*, 2012)	21.0	39	7	(Wols *et al.*, 2012)
Lamotrigine	2	(Keen *et al.*, 2014)	6.8	0.0	6	(Keen *et al.*, 2014)
Lidocaine	10	(Lee *et al.*, 2014)	N/A	N/A		
Losartan	N/A		12.3	13	6	(Starling *et al.*, 2019)

Compound	K_{OH^*} (M^{-1} S^{-1}) x10^9	Reference	ε ($M^{-1}cm^{-1}$) x10^3 @ 254 nm	Φ (mol/einstein) x10^{-3}	pH	Reference
Mefenamic acid	11	(Wols *et al.*, 2012)	5.5	4.7	10	(Wols *et al.*, 2012)
Memantine	6	(Papac *et al.*, 2023)	N/A	N/A		
Metformin	1	(Wols *et al.*, 2014)	0.9	14.0	7	(Wols *et al.*, 2014)
Methylparaben	7	(Zoumpouli et al., 2020)&	14.9	0.7	6	(Alvarez *et al.*, 2020)
Metoprolol	8	(Wols *et al.*, 2012)	0.001	34.7	7	(Wols *et al.*, 2012)
Metronidazole	18	(Wols *et al.*, 2012)	2.1	3.5	7	(Wols *et al.*, 2012)
Nicotine	2	(Hoa *et al.*, 2023)	N/A	N/A		
Ofloxacin	4	(Márquez *et al.*, 2013)	11.9	1.8	7	(Márquez *et al.*, 2013)
Oxazepam	6	(You *et al.*, 2021)	17.5	1.7	7	(You *et al.*, 2021)
Oxycodone	N/A		N/A	N/A		
Paroxetine	10	(Wols *et al.*, 2014)	0.3	210.0	7	(Wols *et al.*, 2014)
Phenazone	8	(Wols *et al.*, 2012)	8.6	33.7	7	(Wols *et al.*, 2012)
Primidone	7	(Wols *et al.*, 2012)	0.2	82.0	7	(Wols *et al.*, 2012)
Propranolol	11	(Wols *et al.*, 2014)	1.3	32.0	3.9-5.5	(Wols *et al.*, 2014)
Ranitidine	15	(Wu *et al.*, 2021)	0.5	12.0	9	(Dong *et al.*, 2017)
Salicylic acid	22	(Milovac *et al.*, 2014)	N/A	N/A		
Sertraline	N/A		0.4	17.0	4 to 9	(Drossou *et al.*, 2022)
Simvastatin	N/A		N/A	N/A		
Sotalol	8	(Wols *et al.*, 2014)	0.4	390.0	7	(Wols *et al.*, 2014)
Sulfamethoxazole	6	(Wols *et al.*, 2014)	13.0	84.0	7	(Wols *et al.*, 2014)
Thiabendazole	N/A		11.0	2.3	5	(Ibarz *et al.*, 2016)
Tramadol	6	(Zimmermann *et al.*, 2012)	N/A	N/A		
Trimethoprim	6	(Wols *et al.*, 2012)	2.9	1.2	7	(Wols *et al.*, 2012)
Valsartan	10	(Zoumpouli *et al.*, 2020)	N/A	N/A		
Venlafaxine	9	(Wols *et al.*, 2014)	0.4	97.0	7	(Wols *et al.*, 2014)

Table S3. Internal standard compounds used in analyses

1	**4-bromophenol-2,3,5,6-d5_NEG**	**21**	**Rantidine,D6**	**41**	**Dimethyl phthalate-3,4,5,6-d4**
2	Atenelol-D7	22	Tramadol.13C,D3	42	Fluoxetine,D5
3	Atorvastatin, D5	23	Trimethoprim,D9	43	Heroin-d10
4	Azithromycin, D3	24	Trimethoprim,D9_2	44	Irbesartan,D7
5	Bezafibrate,D4	25	Venlafaxine	45	Isoproturon,D3
6	Caffeine_13C3	26	Citalopram, D4	46	Mefenamic acid,13 C6
7	Carbamazepine-D10	27	1H-benzotriazole	47	Methadone-D3
8	Ciprofloxacin, D8	28	2-ethyl-hexyl-methoxycinamate	48	Metronidazole-(ethylene)-d4
9	Cis-sertraline, D3	29	4-bromophenol-2,3,5,6-d4	49	Morphine-d3
10	Codeine_D3	30	Acetaminophen-d4	50	Nicotine-d4
11	Diazepam_D5	31	Benzophene-d10	51	Octocrylene,D15
12	Erythromycin-d3-13C	32	Benzyl butyl phthalate-d4	52	Oxybenzone-(phenyl)-d5
13	Furosemide,D5	33	Bis (2-ethylhexyl)phtalate 3,4,5,6-d4	53	Propylparaben,D7
14	Hydrochlorothiazadie,13C,D2	34	Citalopram-d4	54	Sucralose-d
15	Lidocaine-(diethyl),D10	35	DEET, D10	55	Sulfamethoxazole,D4
16	Losartan D4	36	Dibutyl phthalate-d4	56	Triphenyl phosphate-d15(TPHP-d15)
17	Metronidazole-d4	37	Diclofenac,13 C6	57	Tris-2-2chlorocetyl phosphate-d12
18	Naproxen,D3	38	Diclofenac_13 C7		
19	Ofloxacin, D3	39	Diethyl phthalate-3,4,5,6-d4		
20	Oxazepam,D5	40	Dialtiazem,D4		

Table S4. Characteristics of the urine used in experiments

Analysis type	**Value**
Total solids	0.213 g L^{-1}
Volatile solids	0.135 g L^{-1}
pH	6.2 @ 20.8 ºC
Conductivity	11.09 mS @ 20.8 ºC
Total P	0.308 g L^{-1}
Total Ca	0.06 g L^{-1}
Total K	1.061 g L^{-1}
Total Na	1.361 g L^{-1}
Total S	0.287 mg L^{-1}
Total Mg	0.052 g L^{-1}
COD	*10.1 g L^{-1}*
COD after 80 minute UV irradiation	*8.2 g L^{-1}*
Urea-N control urine	*4.50 g L^{-1}*
Urea-N after 80 minute UV irradiation	*3.6 g L^{-1}*
NH4-N control urine	*281 mg L^{-1}*
NH4-N after 80 minute UV irradiation	*223 mg L^{-1}*
Tot-N	*6.12 mg L^{-1}*
Tot-N after 80 minute UV irradiation	*6.10 mg L^{-1}*
NO_3-N control urine	*7.40 mg L^{-1}*
NO_3-N after 80 minute UV irradiation	*13.90 mg L^{-1}*

Table S5 Linearity of calibration points

No.	Compound	R^2	No.	Compound	R^2	No.	Compound	R^2
1	Albuterol (Salbutamol)	0.9976	26	Enzacamene	0.9989	51	Ofloxacin	0.9877
2	Amitriptyline	0.9983	27	Fexofenadine	0.9922	52	Oxazepam	0.9984
3	Amlodipine besylate	0.9935	28	Fluconazole	0.9906	53	Oxycodone	0.9901
4	Amoxicillin	0.9899	29	Fluxetine	0.9906	54	Paroxetine	0.9953
5	Atenelol	0.9974	30	Hydrochlorothiazide	0.999	55	Phenazone	0.9967
6	Atovstatin (Lipitor)	0.9949	31	Ifosfamide	0.9923	56	Primidone	0.9966
7	Azithromycin	0.9937	32	Iopromide	0.995	57	Propranolol	0.9936
8	Bicalutamide	0.9977	33	Irbesartan	0.9614	58	Pyridoxine	0.996
9	Bisoprolol	0.9989	34	Lamotrigine	0.9814	59	Pyrimethamine	0.9969
10	Budesonide	0.9995	35	Lidocaine	0.997	60	Rantidine	0.9982
11	Caffeine	0.9996	36	Loperamide	0.9867	61	Salicilic acid	0.996
12	Carazolol	0.9895	37	Losartan	0.9991	62	Sebacic acid	0.9762
13	Carbamazepine	0.9754	38	Meclofenamic acid	0.9878	63	Sertraline	0.9998
14	Cetirizine	0.9987	39	Mefenamic acid	0.9966	64	Simvastatin	0.9916
15	Chloramphenicol	0.9981	40	Memantine	0.9936	65	Sotalol	0.9984
16	Ciprofloxacin	0.9969	41	Metformin	0.9955	66	Sparofloxacin	0.9655
17	Citalopram	0.9902	42	Methylparaben	0.9828	67	Sulfamethoxazole	0.9991
18	Clatihromycin	0.9904	43	Metoprolol	0.9968	68	Sulindac	0.9944
19	Clopidogrel	0.9929	44	Metronidazole	0.9834	69	Sulisobenzone	0.9906
20	Clozapine	0.9957	45	Metronidazole-OH	0.9923	70	Tamoxifen	0.9893
21	Codeine	0.9966	46	Mirtazapine	0.9865	71	Thiabendazole	0.9988
22	DEET	0.9845	47	Nicotine	0.9997	72	Tramadol	0.9947
23	Diazepam	0.9928	48	Nilfumic acid	0.9808	73	Trimethoprim	0.9934
24	Diclofenac	0.9948	49	Norfloxetine	0.9989	74	Valsatran	0.9959
25	Diltiazepam	0.9997	50	O-desmethylvenlafaxine	0.998	75	Venlafaxine	0.9997

Table S6 Limit of quantification of target OMPs

No.	Compound	LOQ (μg L^{-1})	LOQ (nM)	No.	Compound	LOQ (μg L^{-1})	LOQ (nM)	No.	Compound	LOQ (μg L^{-1})	LOQ (nM)
1	Albuterol (Salbutamol)	0.03	0.13	26	Enzacamene	0.15	0.61	51	Ofloxacin	0.25	0.69
2	Amitriptyline	0.32	1.15	27	Fexofenadine	0.14	0.28	52	Oxazepam	0.05	0.18
3	Amlodipine besylate	0.10	0.26	28	Fluconazole	0.25	0.82	53	Oxycodone	0.87	2.76
4	Amoxicillin	0.09	0.24	29	Fluoxetine	0.74	2.39	54	Paroxetine	0.25	0.76
5	Atenolol	0.13	0.49	30	Hydrochlorothiazide	0.05	0.17	55	Phenazone	0.10	0.55
6	Atovastatin (Lipitor)	0.21	0.38	31	Ifosfamide	1.20	4.61	56	Primidone	4.40	20.17
7	Azithromycin	2.60	3.47	32	Iopromide	0.07	0.09	57	Propranolol	0.11	0.42
8	Bicalutamide	0.08	0.17	33	Irbesartan	0.25	0.58	58	Pyridoxine (Vitamin B6)	0.12	0.70
9	Bisoprolol	0.14	0.43	34	Lamotrigine	0.11	0.43	59	Pyrimethamine	0.95	3.82
10	Budesonide	0.46	1.07	35	Lidocaine	0.19	0.81	60	Ranitidine	2.70	8.60
11	Caffeine	0.03	0.13	36	Loperamide	0.85	1.78	61	Salicylic acid	5.50	39.86
12	Carazolol	1.00	3.35	37	Losartan	0.06	0.14	62	Sebacic acid	0.16	0.80
13	Carbamazepine	0.11	0.47	38	Meclofenamic acid	3.40	11.53	63	Sertraline	1.60	5.25
14	Cetirizine	0.02	0.06	39	Mefenamic acid	0.26	1.08	64	Simvastatin	0.06	0.15
15	Chloramphenicol	0.55	1.71	40	Memantine	0.25	1.39	65	Sotalol	0.02	0.07
16	Ciprofloxacin	0.11	0.33	41	Metformin	0.07	0.50	66	Sparfloxacin	0.07	0.17
17	Citalopram	0.12	0.36	42	Methylparaben	1.80	11.84	67	Sulfamethoxazole	1.80	7.11
18	Clarithromycin	0.05	0.07	43	Metoprolol	0.02	0.07	68	Sulindac	0.14	0.38
19	Clopidogrel	0.07	0.23	44	Metronidazole	0.87	5.08	69	Sulisobenzone	0.43	1.40
20	Clozapine	0.01	0.03	45	Metronidazole-OH	0.17	0.92	70	Tamoxifen	0.15	0.40
21	Codeine	0.89	2.97	46	Mirtazapine	0.04	0.14	71	Thiabendazole	0.18	0.90
22	DEET	0.16	0.84	47	Nicotine	0.16	0.99	72	Tramadol	0.13	0.49
23	Diazepam	0.12	0.42	48	Niflumic acid	0.13	0.47	73	Trimethoprim	0.24	0.83
24	Diclofenac	0.57	1.93	49	Norfluoxetine	0.16	0.54	74	Valsartan	1.20	2.76
25	Diltiazem	0.03	0.07	50	O-Desmethylvenlafaxine	0.13	0.49	75	Venlafaxine	0.98	3.54

Table S7 Target OMP concentration in Blank controls and control urine samples

Compounds	LOQ (µg L^{-1})	Untreated water (µg L^{-1})	Blank milliQ water (µg L^{-1})	Lab Blank (µg L^{-1})	Untreated Urine (µg L^{-1})
Albuterol (Salbutamol)	0.03	<LOQ	<LOQ	<LOQ	0.20
Amitriptyline	0.32	<LOQ	<LOQ	<LOQ	<LOQ
Amlodipine besylate	0.10	<LOQ	<LOQ	<LOQ	<LOQ
Amoxicillin	0.09	<LOQ	<LOQ	<LOQ	1.28
Atenolol	0.13	<LOQ	<LOQ	<LOQ	<LOQ
Atovastatin (Lipitor)	0.21	<LOQ	<LOQ	<LOQ	<LOQ
Azithromycin	2.60	<LOQ	<LOQ	<LOQ	<LOQ
Bicalutamide	0.08	0.19	0.40	0.12	<LOQ
Bisoprolol	0.14	<LOQ	<LOQ	<LOQ	<LOQ
Budesonide	0.46	<LOQ	0.62	<LOQ	19.57
Caffeine	0.03	0.03	0.05	<LOQ	2246.32
Carazolol	1.00	<LOQ	<LOQ	<LOQ	<LOQ
Carbamazepine	0.11	<LOQ	<LOQ	<LOQ	<LOQ
Cetirizine	0.02	1.50	1.30	0.34	<LOQ
Chloramphenicol	0.55	<LOQ	<LOQ	<LOQ	<LOQ
Ciprofloxacin	0.11	1.95	0.37	1.07	1.92
Citalopram	0.12	<LOQ	<LOQ	0.13	<LOQ
Clarithromycin	0.05	<LOQ	<LOQ	<LOQ	<LOQ
Clopidogrel	0.07	<LOQ	<LOQ	<LOQ	<LOQ
Clozapine	0.01	0.99	1.83	1.16	0.16
Codeine	0.89	<LOQ	<LOQ	<LOQ	<LOQ
DEET	0.16	0.35	0.28	0.15	1.10
Diazepam	0.12	<LOQ	<LOQ	<LOQ	<LOQ
Diclofenac	0.57	<LOQ	<LOQ	<LOQ	<LOQ
Diltiazem	0.03	0.04	0.07	0.12	<LOQ
Enzacamene	0.15	<LOQ	<LOQ	<LOQ	<LOQ
Fexofenadine	0.14	<LOQ	<LOQ	<LOQ	<LOQ
Fluconazole	0.25	<LOQ	<LOQ	<LOQ	<LOQ
Fluoxetine	0.74	<LOQ	<LOQ	<LOQ	<LOQ
Hydrochlorothiazide	0.05	0.11	0.09	0.09	0.08
Ifosfamide	1.20	<LOQ	<LOQ	<LOQ	<LOQ
Iopromide	0.07	<LOQ	<LOQ	<LOQ	<LOQ
Irbesartan	0.25	<LOQ	<LOQ	<LOQ	<LOQ
Lamotrigine	0.11	<LOQ	<LOQ	<LOQ	0.35
Lidocaine	0.19	<LOQ	<LOQ	<LOQ	<LOQ
Loperamide	0.85	<LOQ	<LOQ	<LOQ	<LOQ
Losartan	0.06	<LOQ	<LOQ	<LOQ	<LOQ
Meclofenamic acid	3.40	<LOQ	<LOQ	<LOQ	<LOQ
Mefenamic acid	0.26	<LOQ	<LOQ	<LOQ	<LOQ
Memantine	0.25	<LOQ	<LOQ	<LOQ	<LOQ
Metformin	0.07	<LOQ	<LOQ	<LOQ	0.60
Methylparaben	1.80	<LOQ	<LOQ	<LOQ	10.35

Compounds	**LOQ (µg L^{-1})**	**Untreated water (µg L^{-1})**	**Blank milliQ water (µg L^{-1})**	**Lab Blank (µg L^{-1})**	**Untreated Urine (µg L^{-1})**
Metoprolol	0.02	0.04	<LOQ	<LOQ	<LOQ
Metronidazole	0.87	<LOQ	<LOQ	<LOQ	<LOQ
Metronidazole-OH	0.17	<LOQ	<LOQ	<LOQ	0.39
Mirtazapine	0.04	0.76	1.04	0.72	0.07
Nicotine	0.16	0.19	<LOQ	<LOQ	49.44
Niflumic acid	0.13	<LOQ	<LOQ	<LOQ	<LOQ
Norfluoxetine	0.16	0.70	<LOQ	<LOQ	1.39
O-Desmethylvenlafaxine	0.13	<LOQ	<LOQ	<LOQ	<LOQ
Ofloxacin	0.25	3.84	0.60	1.11	<LOQ
Oxazepam	0.05	<LOQ	<LOQ	<LOQ	0.39
Oxycodone	0.87	<LOQ	<LOQ	<LOQ	<LOQ
Paroxetine	0.25	<LOQ	<LOQ	<LOQ	<LOQ
Phenazone	0.10	<LOQ	<LOQ	<LOQ	3.09
Primidone	4.40	<LOQ	<LOQ	<LOQ	<LOQ
Propranolol	0.11	0.35	0.21	0.24	<LOQ
Pyridoxine (Vitamin B6)	0.12	<LOQ	<LOQ	<LOQ	1.09
Pyrimethamine	0.95	<LOQ	<LOQ	<LOQ	<LOQ
Ranitidine	2.70	<LOQ	<LOQ	<LOQ	<LOQ
Salicylic acid	5.50	<LOQ	<LOQ	<LOQ	11.64
Sebacic acid	0.16	19.16	6.50	1.32	197.62
Sertraline	1.60	1.96	<LOQ	<LOQ	<LOQ
Simvastatin	0.06	<LOQ	<LOQ	<LOQ	0.23
Sotalol	0.02	<LOQ	<LOQ	<LOQ	0.11
Sparfloxacin	0.07	0.15	0.14	0.12	<LOQ
Sulfamethoxazole	1.80	<LOQ	<LOQ	<LOQ	<LOQ
Sulindac	0.14	<LOQ	<LOQ	<LOQ	<LOQ
Sulisobenzone	0.43	<LOQ	<LOQ	<LOQ	<LOQ
Tamoxifen	0.15	<LOQ	<LOQ	<LOQ	<LOQ
Thiabendazole	0.18	<LOQ	<LOQ	<LOQ	<LOQ
Tramadol	0.13	<LOQ	<LOQ	<LOQ	<LOQ
Trimethoprim	0.24	<LOQ	<LOQ	<LOQ	<LOQ
Valsartan	1.20	<LOQ	<LOQ	<LOQ	<LOQ
Venlafaxine	0.98	<LOQ	<LOQ	<LOQ	<LOQ

Table S8. Internal standard and Target OMP recovery in methanol

Internal standard compounds	Recovery %	Target compound	Recovery %
1H-Benzotriazole-4,5.6,7-d4	94%	Albuterol (Salbutamol)	101%
2-ethyl-hexyl-methoxycinnamate, D15	46%	Amitriptyline	82%
Acetaminophen-d4	95%	Amlodipine besylate	71%
Atenolol, D7	101%	Amoxicillin	104%
Atorvastatin, D5	93%	Atenolol	103%
Azithromycin, D3	157%	Atovastatin (Lipitor)	71%
Bis (2-ethylhexyl) phthalate 3,4,5,6-d4	25%	Azithromycin	100%
Bezafibrate, D4	101%	Bicalutamide	93%
Bis (2-ethylhexyl) phthalate 3,4,5,6-d4	25%	Bisoprolol	100%
Caffeine_13C3	97%	Budesonide	100%
Carbamazepine-D10	99%	Caffeine	104%
Ciprofloxacin, D8	53%	Carazolol	95%
Cis-Sertraline, D3	88%	Carbamazepine	90%
Codeine_D3	112%	Cetirizine	92%
DEET, D10	99%	Chloramphenicol	100%
Diazepam_D5	91%	Ciprofloxacin	90%
Dibutyl phthalate-d4	99%	Citalopram	92%
Diclofenac, 13C6	110%	Clarithromycin	88%
Diethyl phthalate-3,4,5,6-d4	94%	Clopidogrel	76%
Diltiazem, D4	101%	Clozapine	84%
Dimethyl phthalate-3,4,5,6-d4	116%	Codeine	104%
Erythromycin-d3-13C	82%	DEET	84%
Fluoxetine, D5	156%	Diazepam	93%
Furosemide, D5	86%	Diclofenac	83%
Heroine-d9	100%	Diltiazem	88%
Irbesartan, D7	91%	Enzacamene	26%
Isoproturon, D3	97%	Fexofenadine	84%
Lidocaine-(diethyl), D10	102%	Fluconazole	97%
Losartan, D4	90%	Fluoxetine	75%
Mefenamic Acid, 13C6	60%	Hydrochlorothiazide	103%
Methadone-D3	103%	Ifosfamide	95%
Metronidazole-(ethylene)-d4	105%	Iopromide	103%
Metronidazole, D4	104%	Irbesartan	95%
Morphine-d3	114%	Lamotrigine	98%
Nicotine-d4	101%	Lidocaine	103%
Octocrylene, D15	72%	Loperamide	85%
Ofloxacine, D3	93%	Losartan	89%
Oxazepam, D5	98%	Meclofenamic acid	65%
Oxybenzone-(phenyl)-d5	16%	Mefenamic acid	60%
Propylparaben, D7	96%	Memantine	97%
Ranitidine, D6	104%	Metformin	35%
Sucralose-d6	111%	Methylparaben	87%

Internal standard compounds	Recovery %
Sulfamethoxazole, D4	104%
Tramadol, 13C,D3	105%
Trimethoprim, D9	104%
Trimethoprim, D9_2	102%
Triphenyl phosphate-d15 (TPHP-d15)	68%
Tris-2-chlorocetyl phosphate-d12 (TCEP-d12)	109%
Venlafaxine, D6	100%
Average recovery	**93%**
Standard deviation	**26%**

Target compound	Recovery %
Metoprolol	99%
Metronidazole	96%
Metronidazole-OH	102%
Mirtazapine	98%
Nicotine	114%
Niflumic acid	88%
Norfluoxetine	72%
O-Desmethylvenlafaxine	97%
Ofloxacin	97%
Oxazepam	97%
Oxycodone	101%
Paroxetine	67%
Phenazone	100%
Primidone	100%
Propranolol	98%
Pyridoxine (Vitamin B6)	78%
Pyrimethamine	93%
Ranitidine	97%
Salicylic acid	99%
Sebacic acid	102%
Sertraline	73%
Simvastatin	66%
Sotalol	102%
Sparfloxacin	90%
Sulfamethoxazole	90%
Sulindac	96%
Sulisobenzone	87%
Tamoxifen	41%
Thiabendazole	98%
Tramadol	99%
Trimethoprim	99%
Valsartan	97%
Venlafaxine	102%
Average recovery	**90%**
Standard deviation	**16%**

Table S9. Average degradation of Target OMP in water and urine upon different level

Treatment time (min)	%Average degradation				
	UV dose (mJ cm^{-2})	Water	Standard deviation	Urine	Standard deviation
1	*3*	75%	30%	11%	15%
2.5	*6*	82%	27%	11%	12%
5	*13*	93%	17%	14%	15%
10	*26*	95%	16%	19%	18%
20	*52*	97%	13%	27%	24%
40	*103*	98%	10%	41%	31%
80	*206*	99%	4%	55%	36%

Table S10. Calculated *k*-value of target OMPs water and real urine upon 80 min UV irradiation and estimated predicted t_{50}, t_{90} and E_{90} of target OMPs based on *k* values

Compound	UV-treated Water						UV-treated Urine					
	k (min^{-1})	R^2	number of data points used to calculate *k*	t_{50} (min^{-1})	t_{90} (min^{-1})	E_{90} (kWh m^{-3})	*k* (min^{-1})	R^2	number of data points used to calculate *k*	t_{50} (min^{-1})	t_{90} (min^{-1})	E_{90} (kWh m^{-3})
Albuterol (Salbutamol)	0.99	0.87	5	0.70	2.3	1.9	0.0153	0.67	8	45	150	125
Amitriptyline	1.24	0.98	4	0.56	1.9	1.5	0.0108	0.82	8	64	213	178
Amlodipine besylate	5.2*	1.00	2	0.13	0.4	0.4	0.0273	0.83	8	25	84	70
Amoxicillin	1.18	0.96	4	0.59	1.9	1.6	0.0195	1.00	8	36	118	98
Atenolol	0.85	0.96	5	0.81	2.7	2.2	N/A	N/A				
Atovastatin (Lipitor)	5.45	1.00	2	0.13	0.4	0.4	0.0138	0.73	8	50	167	139
Azithromycin	0.11	0.99	5	6.41	21.3	17.7	N/A	N/A				
Bicalutamide	0.88	0.66	5	0.79	2.6	2.2	0.0301	0.95	8	23	76	64
Bisoprolol	0.34	0.59	6	2.05	6.8	5.7	N/A	N/A				
Budesonide	5.4*	1.00	2	0.13	0.4	0.4	0.0263	0.47	8	26	88	73
Caffeine	0.16	0.99	7	4.22	14.0	11.7	N/A	N/A				
Carazolol	5.3*	1.00	2	0.13	0.4	0.4	0.0080	0.90	8	87	288	240
Carbamazepine	0.37	0.99	6	1.85	6.1	5.1	0.0075	0.95	8	92	307	256
Cetirizine	2.88	0.83	3	0.24	0.8	0.7	0.0163	0.92	8	43	141	118
Chloramphenicol	2.75	0.86	3	0.25	0.8	0.7	0.0374	0.96	8	19	62	51
Ciprofloxacin	0.30	0.72	6	2.28	7.6	6.3	0.0117	0.87	8	59	197	164
Citalopram	1.43	0.90	4	0.48	1.6	1.3	0.0071	0.82	8	98	324	270
Clarithromycin	0.37	0.96	6	1.86	6.2	5.2	0.0011	0.66	8	630	2093	1744
Clopidogrel	2.61	0.82	3	0.27	0.9	0.7	0.0646	0.94	8	11	36	30
Clozapine	1.11	0.54	4	0.62	2.1	1.7	N/A	N/A				
Codeine	4.8*	1.00	2	0.14	0.5	0.4	0.0197	0.92	8	35	117	97
DEET	0.65	0.82	5	1.07	3.6	3.0	0.0077	0.97	8	90	299	249
Diazepam	0.81	0.92	5	0.86	2.9	2.4	0.0141	0.99	8	49	163	136
Diclofenac	5.9*	1.00	2	0.12	0.4	0.3	0.0497	0.96	8	14	46	39
Diltiazem	1.39	0.92	4	0.50	1.7	1.4	0.0405	0.99	8	17	57	47
Enzacamene	1.24	0.90	5	0.56	1.9	1.5	0.0529	0.71	8	13	44	36
Fexofenadine	2.84	0.85	3	0.24	0.8	0.7	0.0174	0.94	8	40	132	110

Compound	UV-treated Water						UV-treated Urine					
	k (min^{-1})	R^2	number of data points used to calculate k	t_{50} (min^{-1})	t_{90} (min^{-1})	E_{90} ($kWh\ m^{-3}$)	k (min^{-1})	R^2	number of data points used to calculate k	t_{50} (min^{-1})	t_{90} (min^{-1})	E_{90} ($kWh\ m^{-3}$)
Fluconazole	0.40	0.99	6	1.74	5.8	4.8	0.0047	0.98	8	147	490	408
Fluoxetine	5.3*	1.00	2	0.13	0.4	0.4	0.0182	0.55	8	38	127	105
Hydrochlorothiazide	0.84	0.04	5	0.83	2.7	2.3	0.0394	0.99	8	18	58	49
Ifosfamide	0.12	0.98	7	5.97	19.8	16.5	N/A	N/A				
Iopromide	7.7*	1.00	2	0.09	0.3	0.2	0.0534	0.95	8	13	43	36
Irbesartan	1.42	0.88	4	0.49	1.6	1.4	0.0118	0.88	8	59	195	163
Lamotrigine	0.71	0.96	5	0.98	3.3	2.7	0.0116	0.97	8	60	198	165
Lidocaine	0.15	1.00	7	4.67	15.5	12.9	N/A	N/A				
Loperamide	1.62	0.80	3	0.43	1.4	1.2	0.0161	0.80	8	43	143	119
Losartan	1.49	0.82	4	0.46	1.5	1.3	0.0200	0.98	8	35	115	96
Meclofenamic acid	5.5*	1.00	2	0.13	0.4	0.4	0.0395	1.00	8	18	58	49
Mefenamic acid	2.81	0.75	3	0.25	0.8	0.7	N/A	N/A				
Memantine	0.01	0.96	8	47.48	157.7	131.4	N/A	N/A				
Metformin	5.8*	1.00	2	0.12	0.4	0.3	0.0060	0.75	8	116	384	320
Methylparaben	1.48	0.97	4	0.47	1.6	1.3	0.0013	0.42	8	533	1771	1476
Metoprolol	0.88	0.95	5	0.78	2.6	2.2	0.0013	0.86	8	533	1771	1476
Metronidazole	1.06	0.97	4	0.65	2.2	1.8	0.0461	0.99	8	15	50	42
Metronidazole-OH	1.06	0.96	4	0.66	2.2	1.8	0.0444	0.99	8	16	52	43
Mirtazapine	2.79	0.68	3	0.25	0.8	0.7	0.0554	0.98	8	13	42	35
Nicotine	2.21	0.75	3	0.31	1.0	0.9	0.0108	0.97	8	64	213	178
Niflumic acid	0.62	0.97	5	1.11	3.7	3.1	0.0015	0.50	8	462	1535	1279
Norfluoxetine	5.3*	1.00	2	0.13	0.4	0.4	0.0322	0.90	8	22	72	60
O-Desmethylvenlafaxine	2.74	0.91	3	0.25	0.8	0.7	0.0021	0.93	8	330	1096	914
Ofloxacin	0.43	0.69	6	1.62	5.4	4.5	N/A	N/A				0
Oxazepam	0.89	0.96	5	0.78	2.6	2.1	0.0081	0.98	8	86	284	237
Oxycodone	0.22	1.00	6	3.22	10.7	8.9	0.0235	1.00	8	29	98	82
Paroxetine	1.84	0.90	3	0.38	1.3	1.0	0.0119	0.36	8	58	193	161
Phenazone	7.6*	1.00	2	0.09	0.3	0.3	0.0350	0.98	8	20	66	55
Primidone	0.62	0.97	4	1.12	3.7	3.1	0.0043	0.70	8	161	535	446

Compound	UV-treated Water						UV-treated Urine					
	k (min^{-1})	R^2	number of data points used to calculate k	t_{50} (min^{-1})	t_{90} (min^{-1})	E_{90} (kWh m^{-3})	k (min^{-1})	R^2	number of data points used to calculate k	t_{50} (min^{-1})	t_{90} (min^{-1})	E_{90} (kWh m^{-3})
Propranolol	0.65	0.98	5	1.07	3.6	3.0	0.0034	0.50	8	204	677	564
Pyridoxine	1.55	0.78	4	0.45	1.5	1.2	0.0129	0.91	8	54	178	149
Pyrimethamine	0.13	1.00	7	5.28	17.5	14.6	0.0066	0.94	8	105	349	291
Ranitidine	6.5*	1.00	2	0.11	0.4	0.3	0.0202	0.62	8	34	114	95
Salicylic acid	0.62	0.98	4	1.11	3.7	3.1	N/A	N/A				
Sebacic acid	0.02	0.84	8	36.29	120.6	100.5	N/A	N/A				
Sertraline	0.54	0.95	5	1.28	4.3	3.6	0.0271	0.90	8	26	85	71
Simvastatin	5.3*	1.00	2	0.13	0.4	0.4	0.0540	0.79	8	13	43	36
Sotalol	1.64	0.69	4	0.42	1.4	1.2	0.0216	0.98	8	32	107	89
Sparfloxacin	2.49	0.85	3	0.28	0.9	0.8	0.0559	0.99	8	12	41	34
Sulfamethoxazole	7.4*	1.00	2	0.09	0.3	0.3	0.0404	0.99	8	17	57	47
Sulindac	1.44	0.86	4	0.48	1.6	1.3	0.0411	0.98	8	17	56	47
Sulisobenzone	0.59	0.98	5	1.17	3.9	3.2	N/A	N/A				
Tamoxifen	5.1*	1.00	2	0.14	0.5	0.4	0.1266	0.67	7	5	18	15
Thiabendazole	0.56	0.96	4	1.25	4.1	3.4	0.0109	0.97	8	64	211	176
Tramadol	1.34	0.95	4	0.52	1.7	1.4	0.0037	0.95	8	187	622	519
Trimethoprim	0.20	1.00	6	3.49	11.6	9.7	N/A	N/A				
Valsartan	6.3*	1.00	2	0.11	0.4	0.3	0.0080	0.81	8	87	288	240
Venlafaxine	1.25	0.98	4	0.55	1.8	1.5	0.0016	0.90	8	433	1439	1199

(N/A)- degradation couldn't be modelled as there were no degradation

(*) - conservative k value, actual k values are higher than reported values

t_{50} (min^{-1}) - half time of OMPs spiked based on respective degradation k value

t_{90} (min^{-1}) - half time of OMPs spiked based on respective degradation k value

E_{90} (kWh m^{-3}) - Electricity demand required to remove 90% of OMPs spiked based on respective degradation k value

Table S11. Major functional groups of the 75 OMPs investigated in this study

No.	Compound	Arene	Amine	Alkanol	Alkene	Aniline	Halide	Benzene	Carboximide	Carbonyl	Ether	Ester	Lactam
1	Albuterol (Salbutamol)	+	+	+				+					
2	Amitriptyline	+	+		+			+					
3	Amlodipine besylate	+	+		+		+	+		+	+	+	
4	Amoxicillin	+	+	+				+	+	+			+
5	Atenolol	+	+					+	+	+	+		
6	Atorvastatin	+	+	+			+	+	+	+			
7	Azithromycin		+	+						+	+	+	+
8	Bicalutamide	+		+			+	+	+	+			
9	Bisoprolol	+	+	+				+			+		
10	Budesonide			+	+					+	+		
11	Caffeine	+	+	+									
12	Carazolol	+	+	+				+			+		
13	Carbamazepine	+			+			+		+			
14	Cetirizine	+	+				+	+		+	+		
15	Chloramphenicol	+		+		+	+	+	+	+			
16	Ciprofloxacin	+	+			+		+		+			
17	Citalopram	+	+				+	+			+		
18	Clarithromycin		+	+						+	+	+	+
19	Clopidogrel	+	+				+	+		+		+	
20	Clozapine	+	+		+	+	+	+					
21	Codeine	+	+		+			+			+		
22	DEET	+						+	+	+			
23	Diazepam	+					+	+	+	+			+
24	Diclofenac	+	+			+	+	+	+	+			
25	Diltiazem	+	+					+	+	+	+		+

No.	Compound	Arene	Amine	Alkanol	Alkene	Aniline	Halide	Benzene	Carboximide	Carbonyl	Ether	Ester	Lactam
26	Enzacamene	+			+			+		+			
27	Fexofenadine	+	+	+				+	+	+			
28	Fluconazole	+	+	+			+	+					
29	Fluoxetine	+	+				+	+			+		
30	Hydrochlorothiazide	+	+			+	+	+					
31	Ifosfamide		+				+						
32	Iopromide	+		+			+	+	+	+	+		
33	Irbesartan	+	+				+	+	+	+			
34	Lamotrigine	+	+			+	+	+					
35	Lidocaine	+	+				+	+	+	+			
36	Loperamide	+	+	+			+	+	+	+			
37	Losartan	+	+	+			+	+					
38	Meclofenamic acid	+	+			+	+	+	+	+			
39	Mefenamic acid	+	+			+		+	+	+			
40	Memantine		+										
41	Metformin												
42	Methylparaben	+		+				+		+		+	
43	Metoprolol	+	+	+				+			+		
44	Metronidazole	+	+	+		+							
45	Metronidazole-OH	+	+	+		+							
46	Mirtazapine	+	+			+		+					
47	Nicotine	+	+										
48	Niflumic acid	+	+			+	+	+	+	+			
49	Norfluoxetine	+	+				+	+			+		
50	O-Desmethyl-venlafaxine	+	+	+				+					
51	Ofloxacin	+	+			+	+	+	+	+	+		
52	Oxazepam	+		+			+	+	+	+			+

No.	Compound	Arene	Amine	Alkanol	Alkene	Aniline	Halide	Benzene	Carboximide	Carbonyl	Ether	Ester	Lactam
53	Oxycodone	+	+	+	+			+			+		
54	Paroxetine	+	+				+	+			+		
55	Phenazone	+	+					+					
56	Primidone	+						+	+	+			+
57	Propranolol	+	+	+				+			+		
58	Pyridoxine	+		+									
59	Pyrimethamine	+	+			+	+	+					
60	Ranitidine	+	+		+								
61	Salicylic acid	+		+			+	+	+	+			
62	Sebacic acid									+			
63	Sertraline	+	+				+	+					
64	Simvastatin			+	+					+		+	+
65	Sotalol	+	+	+		+		+					
66	Sparfloxacin	+	+			+	+	+		+			
67	Sulfamethoxazole	+	+			+		+					
68	Sulindac	+			+		+	+		+			
69	Sulisobenzone	+		+				+		+	+		
70	Tamoxifen	+	+		+			+			+		
71	Thiabendazole	+	+					+					
72	Tramadol	+	+	+				+			+		
73	Trimethoprim	+	+			+					+		
74	Valsartan	+	+							+			
75	Venlafaxine	+	+	+				+			+	+	

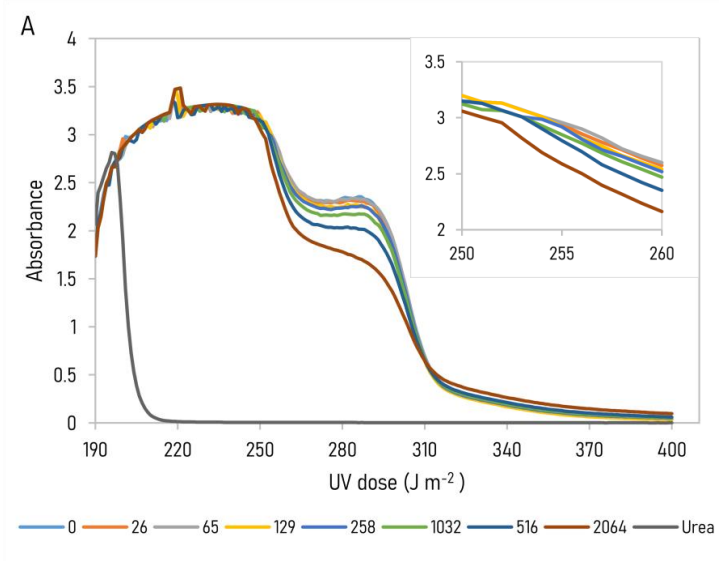
Remark: Functional groups were identified by drawing the chemical structure in an online database (https://epoch.uky.edu/ace/public/fnalGroups.jsp)

Table S12-A Correlation of major functional groups against OMPs degradation in fresh urine

Functional groups	All OMPs	Antibiotics	Antidepressant	Antihypertensive	Beta blockers	NSAIDs	Personal care products
Arene	-0.213	-0.01	-0.38	N/A	N/A	-0.34	N/A
Amine	-0.123	-0.51	0.56	-0.38	N/A	-0.28	0.50
Alkanol	-0.094	-0.55	0.15	0.54	0.11	-0.45	N/A
Alkene	-0.105	0.41	0.24	N/A	N/A	-0.29	-0.50
Aniline	0.109	0.36	0.47	N/A	0.86	-0.23	N/A
Aryl Halide	0.242	0.17	0.42	0.54	N/A	0.27	N/A
Benzene	0.171	0.50	N/A	-0.14	N/A	N/A	0.50
Carboximide	-0.009	0.07	N/A	0.04	N/A	-0.42	N/A
Carbonyl	0.027	-0.16	N/A	0.39	N/A	-0.24	N/A
Carboxylic Acid	0.114	0.39	N/A	0.14	N/A	0.31	-0.50
Ether	-0.164	-0.97	-0.15	-0.37	-0.84	0.04	-0.50
Ester	-0.031	-0.56	N/A	0.38	N/A	N/A	N/A
Ketone	0.024	-0.33	N/A	0.46	N/A	N/A	0.50
Lactam	-0.014	-0.36	N/A	0.47	N/A	N/A	N/A

Table S12-B Correlation of photochemical properties of the 75 OMPs with their degradation in fresh urine

Therapeutic groups	K_{OH^*}	ε	Φ
Antibiotics	0.55	0.08	-0.53
Antidepressant	0.13	0.17	0.19
Antihypertensive	1.00	0.88	0.73
Beta blockers	-0.59	-0.92	0.85
NSAIDs	-0.38	0.31	0.60
Personal care products	N/A	N/A	N/A
All OMPs	0.13	0.36	0.26



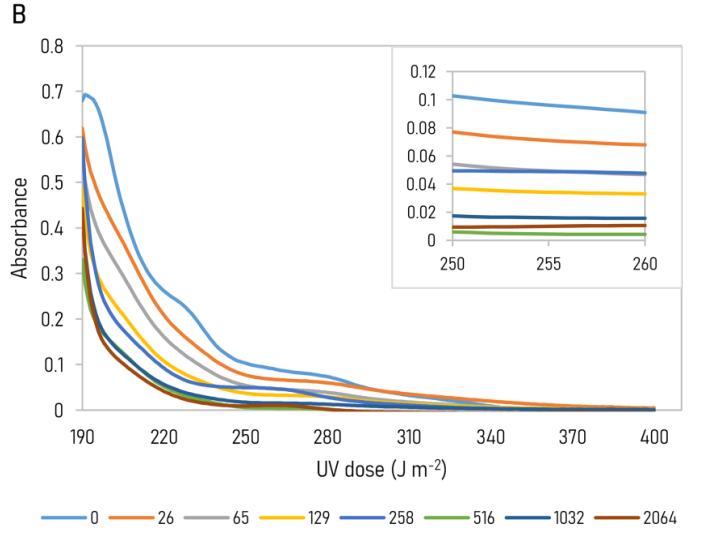


Figure S1. The absorbance of UV-treated samples (A) Urine and (B) water at different UV dose. The number in legend refers to UV dose (J m^{-2}). The absorbance of Urea in MilliQ water with a concentration of 10 g L^{-1}.

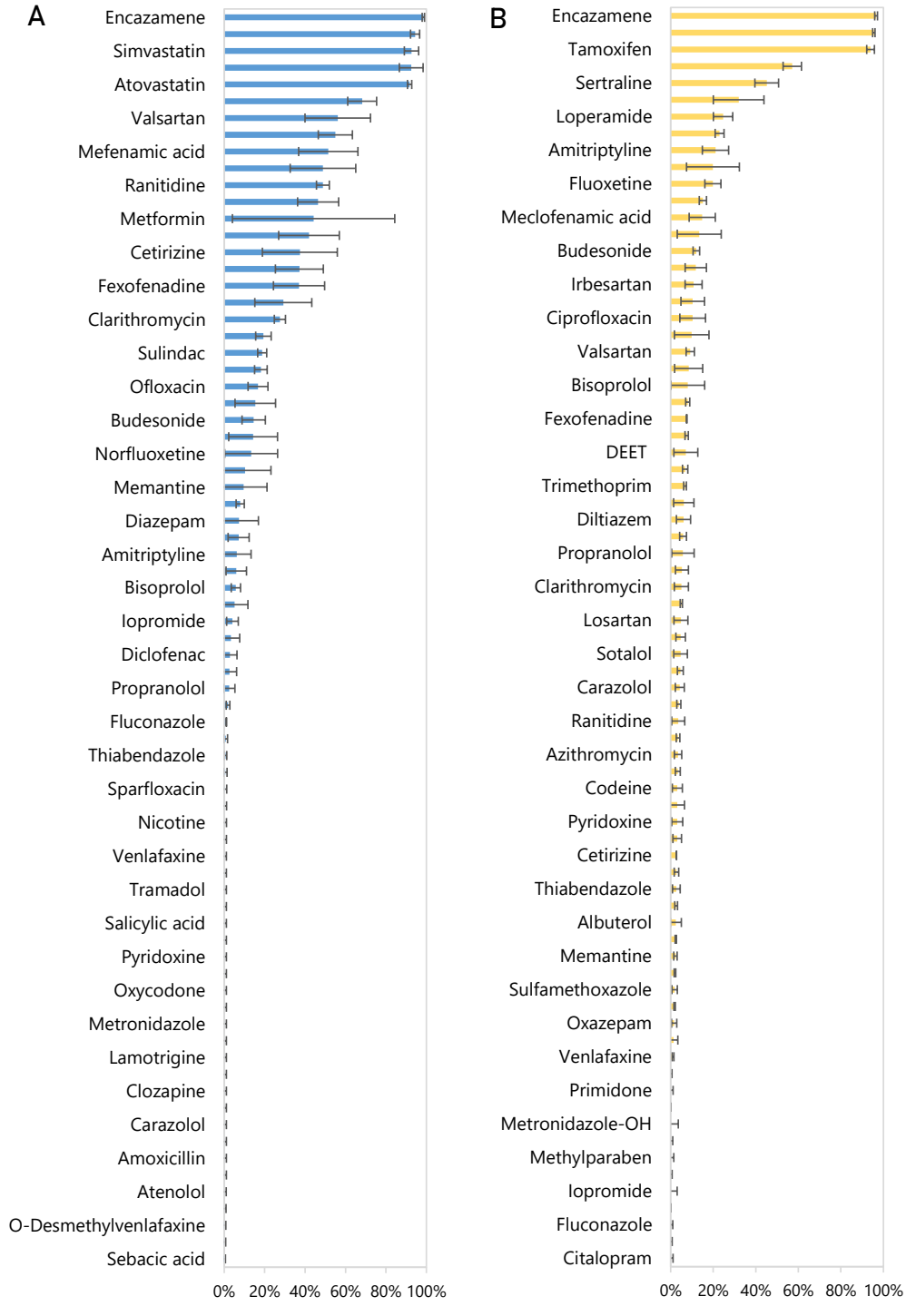


Figure S2. The degradation (%) of 75 OMPs after 80 min Control treatment of water (A) and fresh urine (B). Average values are plotted, and error bars depict the standard deviation (n=3)

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Maximizing the nitrogen recovery during concentrating nutrients in urine by drying is challenged by presence urease enzyme in source separation systems. Furthermore, the presence of micropollutants like pharmaceuticals in urine raises consumer concerns about the acceptability of urine-derived fertilizer. This thesis investigated UV treatment as an alternative nutrient stabilisation and pharmaceutical removal technology from source separated human urine. UV treatment effectively inactivates urease enzyme in urine and reduce pharmaceuticals, demonstrating potential integration in source separation systems for nutrient stabilization and pharmaceutical removal.

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ISSN 1654-9406
ISBN (print version) 978-91-8046-897-8
ISBN (electronic version) 978-91-8046-669-1