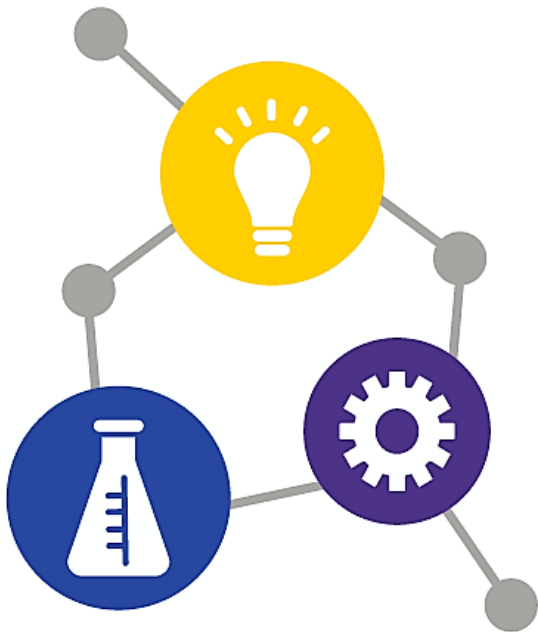February 2022

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Irish Water CRU Water Services Innovation Fund

Investigating novel sensing techniques for monitoring trade effluent (TE)

Commission for Regulation of Utilities (CRU) Water Services Innovation Fund

Investigating novel sensing techniques for monitoring trade effluent (TE)

Attached is *Investigating novel sensing techniques for monitoring trade effluent (TE)* produced for Irish Water by Dr Matthew R Jacobs[a] and Prof Fiona Regan[b] of [a] School of Chemical Sciences and [b] Water Institute, Dublin City University, Glasnevin, Dublin 9, Ireland; and Martin Hogan of JB Barry and Partners Ltd.

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Investigating novel sensing techniques for monitoring trade effluent (TE)

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Report prepared by Dublin City University (DCU) and JB Barry and Partners Ltd

Forward

Industrial manufacturing is reliant on access to water resources for fabrication, synthesis, processing, cleaning and dilution. This usage of water can lead to the accumulation of organic and inorganic compounds in addition to solid particulates producing trade effluent (TE) wastewater. Industry disposes of TE in one of the following ways; (i) containment and transportation to a wastewater treatment plant (WWTP), (ii) released to a sewer network for downstream treatment at a WWTP, or (iii) treated on-site and released to natural waters directly. Of these TE disposal methods, (i) and (ii) are most commonly used to prevent the contamination of natural waters, in line with environmental regulatory requirements. The processes carried out by different industries are highly variable, which leads to similarly variable TE profiles.

Irish Water has a responsibility under statute to licence and monitor trade effluent discharges to the public sewer network in order to protect the environment.

Current TE monitoring approaches use a broad range of methods that are focused on the analysis of physicochemical parameters, nutrients, organics, heavy metals and bacterial loadings. Physicochemical parameters such as flow rate, temperature, and pH are monitored due to the impacts that these parameters have on sewer chemistry and function, coupled with the widespread accessibility and robustness of these sensors. Temperature, for example, can impact the septicity potential of sewers, while excessively high or low pH values can cause corrosion and precipitation of components in the sewer system.

Flow rate, on the other hand, helps inform the loadings of particulates and chemical species emitted to the network. In addition to these measurements, chemical analysis of wastewater is specified in TE licences to demonstrate compliance with specified emission limit values and to provide sewer operators and downstream wastewater treatment plants (WWTPs) with information about the effluent released to the network. Licences are generally constructed by the licensor on the basis of information provided by the Applicant and an observance of both Irish and European environmental standards. The EPA licences certain companies which discharge to the sewer and exceed legal threshold through consultation with Irish Water. These EPA licensed companies and some of the larger trade effluent producers licensed directly by Irish Water produce an annual summary of testing in their Annual Environmental Reports (AERs). The levels of licensed parameters in each of the three specified sectors is

assessed and opportunities for utilizing commercially available sensor and passive sampling technology to measure surrogate parameters of licensed parameters are evaluated.

The potential of surrogate parameters to inform the concentrations and loadings of licensed parameters is evaluated and found to be a promising opportunity for industry, regulators and WWTPs. The variation in TE parameters and their potential to be monitored using surrogates was assessed for three industrial sectors; biopharmachem; food/beverage; and, waste management. Nutrient, organic, inorganic and metallic species were collated with sensor data and compound measurement data using regression and correlations techniques.

From the results obtained in this project there is significant evidence for the potential of spectroscopic, conductivity and turbidity sensors for obtaining surrogate information linked to TE parameters. Additionally, there is opportunity to leverage commercially available ammonia and nitrate sensors to provide additional information regarding nitrogen containing species. Turbidity and spectroscopic measurements at 600, 500 and 450 nm were linked with levels of phosphorous and nitrates in TE species.

Commercially available sensors including pH, turbidity, conductivity, and ion selective electrodes (e.g. ammonia and nitrate) are able to detect bulk differences in the properties of TE that are relevant to TE quality. Sensors may provide valuable capabilities for obtaining real-time information about the composition of TE, without requiring costly and time consuming wet chemistry based analysis, which could be used to provide information about sewer loadings and potential shock loads downstream to waste water treatment plants. The observed data indicate that the site-to-site variation in TE parameters is highly variable and dependent on the specific operations being carried out at each site. Analysis of all-sector TE parameter data suggest that there correlations between COD-turbidity and ammonia-TN. This data provides a valuable insight to the variability and similarities between trades. Valuable data collected in this project suggests that further research and sensor deployments show potential for monitoring TE. Longer deployments would confirm if sensors alone can provide insight into real-time monitoring of industrial TE. Sensor and surrogate should be individually calibrated and validated for each site of interest to provide reliable information on changes in effluent quality.

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Glossary of Terms and Abbreviations

Abbreviation or Term	Definition or Meaning
AER	Annual Environmental Report
AOP	Advanced Oxidation Process
APHA	American Public Health Association
BOD	Biochemical Oxygen Demand
BOD_5	5-day BOD assay
C_{18}	Non-polar octadecyl extraction phase
CD	Conductivity
CN^-	Cyanide anion
CO_3^{2-}	Carbonate
COD	Chemical Oxygen Demand
Corr	Correlation coefficient
d	day
DAF	Dissolved air flotation
DGT	Diffusive gradient thin films
DO	Dissolved oxygen
DPD	*N,N*-diethyl-*p*-phenylenediamine
EPA	Environmental Protection Agency
FOG	Fats, oils, greases
GC	Gas chromatography
h	Hour
H_2O_2	Hydrogen peroxide
H_2SO_4	Sulphuric acid
HCl	Hydrochloric acid
HCO_3^-	Bicarbonate
HLB	Hydrophilic Lipophilic Balance extraction phase
IC	Ion chromatography
ICP	Inductively coupled plasma
ID	Identifier
IED	Industrial emissions directive
ISE	Ion selective electrode
LLE	Liquid-liquid extraction
Max	Maximum
Min	Minimum
MS	Mass spectrometry
NaOH	Sodium hydroxide
NC	Not completed
ND	Not detected
NH_3	Ammonia
NO_2^-	Nitrite
NO_3^-	Nitrate
NTU	Normalised turbidity units
O_3	Ozone
OES	Optical emissions spectroscopy
Organics	Organic carbon species
ORP	Oxidation reduction potential
PAH	Polyaromatic hydrocarbons

PCA	Principle component analysis
pH	Hydrogen activity
PO₄ PO_4	Phosphate (orthophosphate)
POCIS	Polar organic chemical integrative sampler
PS	Passive sampler
S₂⁻ S_2^-	Sulphide
SD	Standard deviation
SO₄²⁻ SO_4^{2-}	Sulphate
SPE	Solid phase extraction
TDS	Total dissolved solids
TE	Trade effluent
TKN	Total Kjeldahl nitrogen
TN	Total nitrogen
TOC	Total organic carbon
TON	Total oxidised nitrogen
TP	Total phosphorous
TRP	Total reactive phosphate
TS	Total solids
TSS	Total suspended solids
UV	Ultraviolet light spectrum
UV-Vis	Ultraviolet-Visible spectrophotometry
Vis	Visible light spectrum
WWTP	Wastewater treatment plant

Non-Technical Summary

Investigating novel sensing techniques for monitoring trade effluent (TE)

Industrial manufacturing is reliant on access to water resources for fabrication, synthesis, processing, cleaning and dilution. This usage of water leads to the accumulation of organic and inorganic compounds in addition to solid particulates producing trade effluent (TE) waste. Industry disposes of TE in one of the following ways; (i) containment and transportation to a wastewater treatment plant (WWTP), (ii) released to a sewer network for downstream treatment at a WWTP, or (iii) released to natural waters with varying levels of treatment. Of these TE disposal methods, (i) and (ii) are most commonly used to prevent the contamination of natural waters, in line with environmental regulatory requirements. The processes carried out by different industries are highly variable, which leads to similarly variable TE profiles.

This research project on investigating novel sensing techniques for monitoring trade effluent (TE) was designed to explore innovative off-the-shelf technologies for monitoring TE from three industrial sectors. Monitoring of TE is currently dependent on offline chemical analysis that is both costly and time consuming. The offline nature of TE monitoring prevents the application of preventative TE management strategies which could improve the outcomes for Irish Water and its customers. Novel technologies provide potential for reducing the monitoring burdens of TE, providing better data for accurate TE management and the potential for more accurate billing of TE are the primary benefits of the project.

The sectors selected for this project are;
a) Biopharmachem – companies involved in the manufacture of biological pharmaceutical products.
b) Food and beverage – companies involved in the manufacture of food and beverage products.
c) Waste management – companies involved in the reception, processing, treatment and disposal of wastes.

These sectors were identified by Irish Water as being among the most significant industrial contributors to sewer networks that can impact the operation of wastewater networks and treatment plants.

The project set out to achieve the following goals to improve wastewater monitoring and management outcomes:
a) Characterise trade effluent from three high risk sectors;
b) Identify markers or surrogate parameters in trade effluent;
c) Investigate applicability of novel sensor technology for monitoring trade effluent.

These goals were achieved by carrying out a characterisation of trade effluent from company's representative of each of the target industrial sectors. Conventional wet chemistry and organoleptic analysis was augmented with a range of advanced analysis techniques to enhance the understanding of TE composition.

The data gleaned from the chemical analysis can be used to estimate the impacts of present and future industrial companies on sewer and wastewater treatment infrastructure. It also provides details on the variation of TE composition over time within the biopharmachem, food/beverage and waste management sectors which can be useful for resourcing and TE management planning. There are immediate direct benefits from the above to Irish Water Customers. These benefits include a more cost-effective management of TE thereby reducing the Irish Water operational cost base as a result of lower monitoring costs and a lower cost of conveyance and treatment of TE due to a reduction in shock loadings from TE.

The results of TE analysis was used to determine which parameters would be the most useful for monitoring the composition of TE using off-the-shelf sensor or passive sampler technologies. The analysis and deployments indicated that a selection of sensor technologies such as turbidity, conductivity, pH, chloride, ammonia, nitrite, and nitrate provide useful insight into TE composition that inform TE properties in real-time.

The data obtained from this chemical characterisation sought to identify the levels of commonly monitored species within TE, to determine which targets may be of interest for sensor or passive sampling monitoring.

It was found that:

- The levels and variation of COD, TOC, nutrients and ionic species indicate that the organic and inorganic components of TE are present at levels amenable to sensor, spectroscopic and passive sampling monitoring.

- Testing with conductivity and turbidity sensors indicate that these commercially available sensors are able to detect bulk differences in the properties of TE samples that may provide insight into changes in TE composition.

- While conductivity and turbidity measurements have low selectivity for specific targets such as COD or ammonia, knowledge about the composition of specific sectors or sites is important for correlating changes in these sensors with specific monitored parameters.

- Commercial sensors for ammonia, nitrite, and nitrate are available and ammonia sensors are of particular interest due to the variation that this species shows in the biopharmachem, food/beverage and waste management sectors.

- Regression between conductivity measurements and chloride levels revealed a significant link between the two parameters with a moderate association (R^2 = 0.743). This suggested that conductivity may serve as a useful surrogate for chloride levels.

The data obtained on the composition of TE samples can be used to inform levels of input to sewer systems and the selection of sensor and passive sampler technologies for monitoring TE properties. Furthermore, this comprehensive data set enables the identification of appropriate markers, or surrogate species, for monitoring licensed parameters within TE. The chemical characterisation information identified the levels of commonly monitored species within TE to determine which analytes may be of interest for sensor or passive sampling monitoring.

From the results obtained there is significant evidence for the potential of spectroscopic, conductivity and turbidity sensors for obtaining surrogate information linked to TE parameters. Spectroscopic sensors at UV-vis absorbance's 254 nm and 280 nm were shown to co-vary with COD, TOC and phosphates in TE samples.

It is proposed that the monitoring burden for companies can be reduced based on a more nuanced approach to sampling based on risk. This can be achieved using passive sampling approaches tailored for certain chemical groups for example nutrients or organic compounds.

Future research into the cost effectiveness of various sensor technologies compared with conventional TE monitoring would prove highly valuable to both industry and Irish Water. Additionally, research into the recovery of nitrogen and phosphorous materials may prove a valuable opportunity to extracting additional value from TE by facilitating the development of circular economies. The results suggest real value in sensor-based monitoring of TE and potential for use of targeted passive sampling approaches to refine the information that can be obtained.

1

Review of current monitoring approaches of effluent water quality in industry

Review of current monitoring approaches of TE in industry

Introduction

Industrial manufacturing is reliant on access to water resources for fabrication, synthesis, processing, cleaning and dilution. This usage of water leads to the accumulation of organic and inorganic compounds in addition to solid particulates producing trade effluent (TE) waste. Industry disposes of TE in one of the following ways; (i) containment and transportation to a wastewater treatment plant (WWTP), (ii) released to a sewer network for downstream treatment at a WWTP, or (iii) released to natural waters with varying levels of treatment. Of these TE disposal methods, (i) and (ii) are most commonly used to prevent the contamination of natural waters, in line with environmental regulatory requirements. WWTPs are designed to ensure that the return of water to natural systems does not compromise the quality of rivers, lakes or marine environments (Prasse et al., 2015). However, WWTPs can face significant challenges in eliminating the wide variety and variable loadings of anthropogenic contaminants derived from domestic, (commercial) and industrial sources (Petrie et al., 2015). While the content of wastewater delivered to WWTPs via transportation is sometimes well specified by the company shipping the waste, the contents of sewer derived TE varies based on the industrial and urban sources connected to the sewer system, presenting plant operators with additional challenges. Sewer systems are critical wastewater transport networks that are designed under normal conditions to provide low cost transfer of TE and urban wastewater to WWTPs, while preventing the release of untreated wastewater to the natural environment. Since downstream treatment is performed to reduce the order of contaminants prior to release of water back to the environment, the primary concern of sewer and WWTP operators is to ensure the integrity of sewer networks and to characterise the properties of wastewater for WWTP operation and management purposes. Excessive levels of organic/inorganic species or high particulate loadings can damage sewer networks, and negatively impact the operation of WWTP facilities. Large volumes of wastewater are generated by urban centres from domestic and commercial sources. Industrial operations sometimes produce high volumes of effluent or effluent that contains significant levels of compounds/particles that can impact sewer networks and downstream processing, which has led to regulators controlling industrial inputs to sewer systems via TE

licences. Irish Water has a responsibility under statute to licence and monitor trade effluent discharges to the public sewer network under Section 16 of the 1977 Water Pulltion Act in order to protect the environment. (The EPA licence industries who discharge wastewater to public sewers exceeding thresholds under the IED directives; Irish Water are a statutory consultee in this process). The monitoring of industrial TE is typically carried out using organoleptic, wet chemistry and other analysis techniques requiring significant analytical resources and technical expertise.

The processes carried out by different industries are highly variable, which leads to similarly variable TE profiles. For example, waste management companies can receive waste from commercial, domestic and industrial sources with inputs from agricultural activities, construction/demolition, chemical waste, electronics, food waste, green/brown waste, mining waste, packaging, scrap metal and more. Waste management companies focused on scrap metal or recyclables processing may use water during processing, which necessitates the monitoring of these species in TE (Fallahzadeh et al., 2017; Kavcar et al., 2009). In the case of landfill or composting based waste management, leachate is monitored for levels of metals or organics that could impact sewer or WWTP treatment downstream. Biopharmaceutical companies invest significant resources in the preparation and recovery of water-soluble drugs/biotherapeutics that were produced by chemical synthesis or using biotechnology cell culture strategies. Biopharmachem waste can contain organic matter such as organic compounds (e.g. solvents, proteins, sugars and buffers) and salts that can impact sewers and downstream wastewater treatment depending on the loadings. Similarly, food and beverage companies can produce TEs that contain organic and inorganic compounds along with particulate matter that can cause or contribute to sewer blockages.

Regulatory (licensing) and economic incentives (charging) are used in many jurisdictions to encourage industry to use a range of strategies to reduce the loading of organic, inorganic and particulate loadings that they output as TE (Gadipelly et al., 2014; Gao et al., 2015; Valta et al., 2015). Physicochemical methods for reducing particulate loadings include a range of sedimentation, coagulation, flocculation, and filtration techniques, while organic and inorganic species can be precipitated by

manipulation of effluent pH and the addition of various reagents (Prasse et al., 2015). Biological treatments utilise bacterial processes to degrade contaminants without the need for high energy consumption (Song et al., 2018). Biological strategies utilise either anaerobic or aerobic bacteria in a reactor setup optimised for the elimination of bulk organic and inorganic species. Advanced oxidation processes (AOP) utilise a combination of ultraviolet radiation and free radical oxidation chemistry (UV/H_2O_2, UV/O_3), which provides capacity for the degradation of organic compounds and bacteria that may be present in TE. In addition to reducing the levels of species relevant to TE licenses, the recovery of certain components of TE can provide significant value to industry, for example processing of TE can yield biogas that can be used to produce energy (Arashiro et al., 2018), or resources such as metals, ammonia, nitrate or phosphate can be extract as a side product (Song et al., 2018; Zhao et al., 2018).

Current TE monitoring approaches use a broad range of methods that are focused on the analysis of physicochemical parameters, nutrients, organics, heavy metals and bacterial loadings. Physicochemical parameters such as flow rate, temperature, and pH are monitored due to the impacts that these parameters have on sewer chemistry and function, coupled with the widespread accessibility and robustness of these sensors. Temperature, for example, can impact the septicity potential of sewers, while excessively high or low pH values can cause corrosion and precipitation of components in the sewer system. Flow rate, on the other hand, helps inform the loadings of particulates and chemical species emitted to the network. In addition to these measurements, chemical analysis of wastewater is specified in TE licences to provide sewer operators and downstream WWTPs with information about the effluent released to the network. The species monitored during chemical analysis are dependent on the nature of the water use for each industry, however the main parameters that are monitored include biological oxygen demand (BOD), chemical oxygen demand (COD), along with inorganic ions (sodium, chloride, and sulphate), inorganic nutrients (phosphate, nitrate and ammonia), heavy metals and organics. The tests currently employed for chemical analysis of these targets are expensive, time consuming and require specialist expertise, which limits the monitoring capabilities of both industry and regulators.

Sensor and passive sampling technologies could provide useful alternatives to these chemical assays. Low cost sensors provide the capacity to obtain real-time information about the composition of TE that can be correlated with regulated parameters. For example, turbidity, oxidation reduction potential (ORP) and conductivity probes can provide insight into the particulate, inorganic and organic loadings of TE (Gholizadeh et al., 2016). Passive sampling provides capacity to measure time-weighted averages of licensed parameters to provide a better representation of the output from industry to sewers without requiring extensive and costly sampling campaigns that would otherwise be required. Real-time monitoring represents a paradigm shift that could improve the capabilities of industry to control the properties of TE released to sewer, providing that these technologies can be deployed at reasonable costs and provide the performance required (Chung and Yoo, 2015; Prasse et al., 2015; Roll and Halden, 2016; Zhuiykov, 2012). Present European regulations do not specify that continuous monitoring of any parameters is required, however given the low cost of current generation sensor technology this may change in the future (Allan et al., 2006).

This review presents a critical analysis of the current practices utilised for monitoring the physical and chemical components of TE industrial sectors; (i) biopharmachem, (ii) food and beverage, and (iii) waste management industries. These sectors have been identified as representing specific risks to sewer networks and downstream WWTPs in Ireland, due their capacity to potentially deliver shock loads of licensed parameters.

Licences are generally constructed by the licensor on the basis of information provided by the Applicant and an observance of both Irish and European environmental standards. The EPA licences certain companies which discharge to the sewer. These EPA licensed companies produce an annual summary of testing in their Annual Environmental Reports (AERs). The levels of licensed parameters in each of the three specified sectors is assessed. Opportunities for utilising commercially available sensor and passive sampling technology to measure surrogate parameters of licensed parameters are evaluated.

The potential of surrogate parameters to inform the concentrations and loadings of licensed parameters is evaluated and found to be a promising opportunity for industry, regulators and WWTP operators.

Monitoring industrial TE

The monitoring of TE has a number of considerations, including the frequency of sampling and the analytical techniques used for obtaining robust measurements of the required licensed parameters. AERs report time averaged pH, flow and temperature data along with specified chemical measurements that are relevant to their respective industry licenses. Data are reported either as monthly or yearly averages with indications on whether an exceedance was measured during the period covered by the report.

Sample collection and preparation

The sampling method, frequency and sample preparation are critical elements to consider in any analysis. It has been shown that the precision of modern analytical methods is excellent compared with the inter-sample uncertainty due to the variability in wastewater samples (Roll and Halden, 2016). As a result of this variability, the challenge of obtaining a representative sample is still an unresolved issue that can introduce measurement uncertainty. Various sampling strategies are outlined in Table 1. The simplest of the sampling methods is grab sampling, where a volume of water is collected at a discrete point in time and then analysed either at the point of sampling, transported or stored for later analysis. Grab sampling provides a snapshot of the chemical composition of a TE sample at a specific time point; however, the composition of TE can vary over short time scales depending on the processes being carried out by an industry site. As a result of this variability, grab sampling is rarely representative of the TE outputted from a site (Allan et al., 2006; Novic et al., 2017). Composite sampling strategies are often implemented to overcome this limitation of grab sampling, which involves collecting a series of samples at different time points and combining them in to a single "composite" sample to provide a time averaged sample. This procedure goes some way to increasing the representativeness of a sample, as the composition of the final sample contains portions of TE from a range of time potions over which the sample was collected. Composite sampling reduces the

number of samples that must be analysed compared to grab sampling, however it introduces a latency period between sample collection and measurement which limits the ability of industrial sites to control the properties of their TE before release to sewer. Furthermore, TEs can also undergo degradation over time when held in a sampling container, which introduces an additional complication for composite sampling.

Table 1 Sampling techniques for TE monitoring

Measure-ment	Advantages	Disadvantages
Grab sample	Simplest sample regime	Time averaged information not available without collecting and analysing a large number of samples
	Accurate quantification possible	Resource and labour intensive for high frequency sample analysis
	Can be combined with sample enrichment techniques such as solid phase extraction (SPE) and liquid-liquid extraction (LLE)	Event detection limited speed of analysis
	Maintenance free	
Composite	Provides time weighted averages of TE composition	Sampling over a long duration introduces a latency period between sample collection and analysis
	Reduces resources required to obtain a time weighted average compared to grab sampling	Requires a composite sampling device, or labour intensive sample collection
	Can be combined with sample enrichment techniques such as SPE and LLE	Event detection limited by sample collection interval and speed of analysis
	Minimal maintenance required	Degradation of sample can occur over time without adequate sample storage (e.g. refrigeration)
	Useful for regulatory analysis. Provides representative information on TE composition over period of sampling	
Passive sampling	Provides time weighted averages of TE composition	Calibration procedure requires technical skills
	A range of passive samplers are available for selective measurements of target compounds	Event detection limited by sample deployment interval and speed of analysis
	Selective for target analytes of interest	Can only capture the soluble fraction of analytes
	Provides representative information on TE composition over period of deployment	
Sensors	Real time monitoring	Periodic sensor maintenance required
	Event detection possible	Limited sensitivity for some targets, analyte preconcentration not easily achievable
	Trend analysis capabilities	Complex sensor responses due to the complexity of TE
	Simple data collection and calibration possible with commercial data logging equipment and wireless technology	

Passive sampling (Mills et al., 2014; Sonavane et al., 2018; Vrana et al., 2005) and real-time monitoring strategies with sensors (see section 2.3) have been developed to overcome the limitations of grab and composite sampling regimes that can neglect short term release events (Kara et al., 2016; O'Flynn et al., 2010). Passive sampling technology provides the capacity to continuously sample wastewater *in situ* by accumulating analytes from the aqueous phase of TE onto an adsorbent material. Passive samplers can be operated in either of two regimes as shown in Figure 1. In the case of the kinetic regime, analytes are accumulated in the adsorbent receiving phase of the passive sampler over the duration of the samplers' deployment. In the case of an analyte that is present at a consistent concentration, the mass adsorbed onto the passive sampler will accumulate linearly, and a time weighted average can be obtained by dividing the total accumulated mass by the duration of deployment. If a passive sampler is deployed for a duration long enough for the concentration of the target analyte to reach equilibrium with the surrounding aqueous phase, then the concentration of that species in the aqueous phase can be measured for the time point corresponding to the time the sampler was removed from deployment.
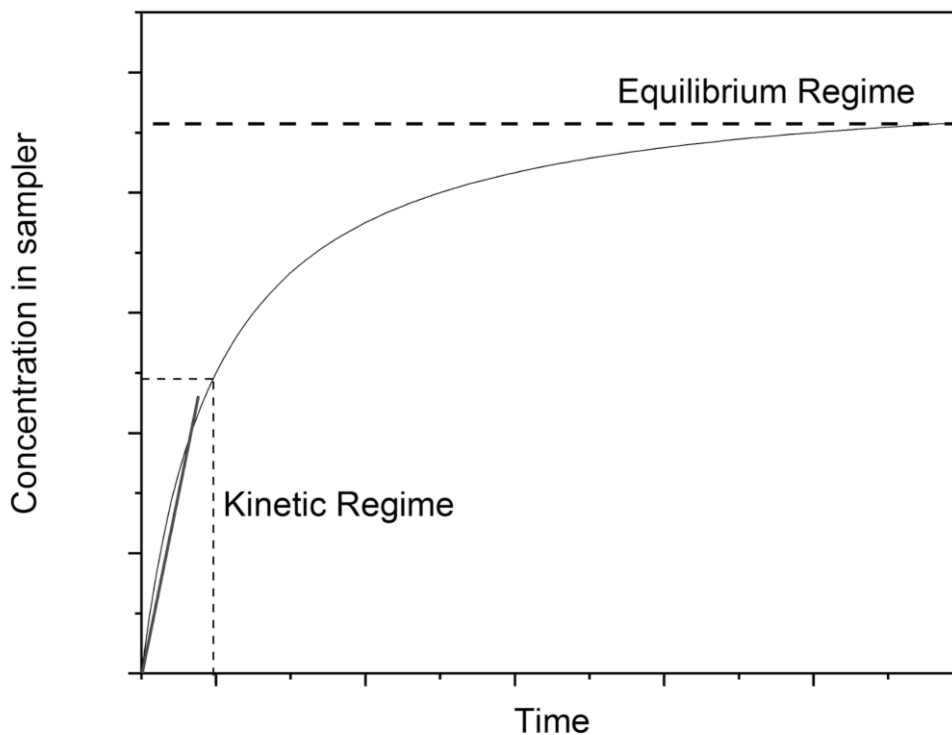
Figure 1 Passive sampling devices adsorb compounds from the aqueous phase and operate in two regimes (Vrana et al., 2005). In the kinetic regime, compounds are linearly absorbed as a function of time into the device. Once the concentration of the species in the sampler reaches the concentration of the surrounding water the equilibrium regime is obtained

A variety of passive sampler formats have been developed for example the polar organic chemical integrative sampler (POCIS) (Alvarez et al., 2004), Chemcatcher (Kingston et al., 2000; Charriau et al., 2016; Lissalde et al., 2016) and diffusive gradient thin films (DGT) (Davison and Zhang, 1994). These passive sampling technologies have been shown to provide capacity for robust analysis of a range of compounds including licensed parameters such as organic and inorganic nutrients species (Knutsson et al., 2013), metals (Zhang and Davison, 1995) and other organic compounds (Kaserzon et al., 2014). Passive sampling technology has been successfully applied in industrial settings to monitor biopharmachem and waste management industries (Ahrens et al., 2015; Mills et al., 2014; Sultana et al., 2017), and should also be viable as a monitoring tool in the food and beverage sector (Valta et al., 2015).

While passive sampling and use of sensors do not currently meet the regulatory sampling and testing requirements specified in the relevant regulations, they offer alternative cost-effective means of monitoring TE to allow both industry and water services authorities better manage TE.

Physical and chemical analysis

Analysis of TE samples requires a range of sample preparation techniques to reduce physical and chemical interferences present that complicate the measurement of licensed parameters (American Public Health Association et al., 2017). For example, particulates can block separation columns reducing chromatographic performance (Morrison and Dolan, 2005; Pfannkoch, 2014), they can coat sensors and electrodes impeding electrode responsivity (Crespo, 2017) and cause light scattering that is detrimental to fluorescence and absorbance measurements (Baurès et al., 2007). Filtration is ubiquitously used to reduce the impacts that particulates can have on analysis, however this of course leads to a loss of information since the particulates are removed prior to analysis. Digestion reactions and the use of organic solvents can facilitate the dissolution of particulates and solids present in TE, making them amenable towards chemical analysis. In particular, digestions are extensively used for the preparation of TE samples in the case of bulk nutrient measurements (*e.g.* COD, TOC, TN and TP analysis) and along with metals analysis where an acid digestion procedure is normally performed to solubilise metals within particulates (American Public Health Association et al., 2017). Similarly, liquid-liquid extraction (LLE) and SPE are useful for the separation of organic, inorganic and metallic analytes present in complex samples prior to measurement (Andrade-Eiroa et al., 2016a, 2016b; Carasek et al., 2018).

Despite the wide variation in industrial TEs, there are many physical and chemical analyses that are consistently performed due to the standardisation of environmental regulations that are applied to industry. Regulators specify the measurements that each industrial enterprise must adhere to, and they may also publish, specify, or recommend methods and best practices required to adhere to their regulations. The most prominent resource cited for TE monitoring is Standard Methods for the Examination of Water and Wastewater that is maintained by the American Public Health Association which contains a compendium of information on the analysis of water (American Public Health Association et al., 2017).

Some of the most important parameters used in the course of monitoring TE are summarised in Table 2. Organoleptic parameters provide general information on the presence of organic or inorganic species in water, for example the presence of discolouration is suggestive of the presence of metallic or organic species. Assessments of colour or odour are generally subjective in nature although efforts to formalise the assessment of these parameters are ongoing using techniques such as gas chromatography (GC) often with mass spectrometry (MS) (Barczak and Kulig, 2017; Chin et al., 2017) and electronic nose technology (Blanco-Rodríguez et al., 2018). Quantitative determinations of physical parameters such as turbidity and solid content provide valuable objective information on the properties of TE that can inform quality. Turbidity is derived from measurement of the light scattered by a sample, which is determined by the number of particles and their respective sizes as well as light absorbance interferences. Measurements of solids in TE are carried out by weighing the mass solids remaining after evaporation of a specified quantity of effluent, which provides a measure of the total suspended solids (TSS). The addition of a filtration step prior to the evaporation step will provide complementary information about the amount of total dissolved solids (TDS) present in TE that are not be removed using typical filtration strategies. Suspended solids contribute to the turbidity of TE which is correlated with organic loads in TE (Thomas et al., 1997).

Analysis of chemical species within TE streams can be achieved by a range of spectroscopic, colorimetric, titrimetric and electrochemical techniques as outlined in Table 2. Many of the techniques described in the Standard Water Analysis Guidelines (American Public Health Association et al., 2017) require substantial analytical expertise to obtain satisfactory results, however commercially available analytical kits have been developed to simplify the analysis of many parameters. Aggregate chemical measurements are invaluable for monitoring the bulk properties of TE.

Of these parameters COD is perhaps the most important for TE monitoring that quantifies the capacity of the organic and inorganic components of a sample that can undergo chemical oxidation (Geerdink et al., 2017; Li et al., 2018). The dichromate anion ($Cr_2O_7^{2-}$) is used as a standard oxidizing agent, and its reaction with organic and inorganic species can be quantified to determine the number of oxygen equivalents consumed. COD primarily informs on the presence of organic species that are dominant in TE, although it does not distinguish between organic and inorganic compounds. Sample digestion at high temperatures is required, which means that losses of volatile organic species are possible in open reflux conditions, however the use of closed reactors can prevent these losses (American Public Health Association et al., 2017). The measurement of the equivalents of dichromate consumed during an experiment is ascertained either by direct spectrophotometric measurements of the chromium (III) anion which is the reduction product of the chromium (VI) anion, or titrimetric techniques by back titration with ferrous ammonium sulphate.

Total organic carbon (TOC) is another useful measure of the amount of organic carbon present in samples by the conversion of organic carbon to carbon dioxide (Bisutti et al., 2004). This conversion can be achieved either by oxidation at high temperatures in the presence of oxygen and an appropriate catalyst, or with milder conditions using ultraviolet irradiation combined with chemical oxidation. Carbon dioxide is then quantified using spectroscopy, coulometric, or conductivity-based techniques. TOC analysers are commercially available that have the capacity for automated sampling and analysis, simplifying the measurement and increasing sample throughput, however these instruments require a significant capital investment and expertise in operational input. Some of the information captured in a TOC measurement is incorporated into the COD or BOD measurements hence these parameters have some surrogacy for one and other.

BOD measures the oxygen consumption rate of biochemical species present in a sample. This test is typically performed using a 5-day assay (BOD_5) where the dissolved oxygen level of a sample is measured, after which the sample is hermetically sealed for a 5-day duration after which the dissolved oxygen level is measured to determine consumption of oxygen as a function of time (Jouanneau et al., 2014). Oxygen is consumed by both carbonaceous and nitrogenous species however, for purposes of TE analysis, nitrogenous oxygen demand is often suppressed by the addition of an inhibitor such as 2-chloro-6-(trichloromethyl) pyridine, and nitrogenous species are then quantified separately. The long duration required to complete a BOD_5 measurement is a substantial limitation on this assay (Jouanneau et al., 2014), however the information provided by this parameter is important for controlling organics

and as a result there is a substantial research focused on the estimation of BOD_5 from sensor and other chemical analysis and sensor data (Reshetilov et al., 2013).

Digestion techniques, like those applied during the COD and TOC methods, have been developed for quantifying the total amounts of nitrogen and phosphorous along with subclasses of these species. Sample digestion is a method of reducing the complexity of a sample by converting the vast number of compounds into a form that is amenable towards direct analysis saving time on separation, however sample digestion is an additional sample preparation step that is costly in terms of time and resources.

Nitrogen can be divided into five main classes including total nitrogen (TN), ammonia (NH_3), nitrate (NO_3^-), nitrite (NO_2^-) and organic nitrogen (Kjeldahl nitrogen). TN is useful for informing the overall nutrient loading of an effluent stream due to the biochemical activity of this species that can contribute to bacterial growth in natural systems. Ammonia is amenable to direct measurement either by ion selective electrode technology (Huang et al., 2019) or by colorimetric techniques that are amenable to flow injection analysis setups (Y. Xie et al., 2016). Nitrate and nitrite are common species present in TE since these species have been incorporated into inorganic fertilizers and food additives along with being products of industrial processes (Moorcroft et al., 2001). Nitrate can be formed from nitrite by *in vivo* reduction and is implicated with impaired cellular function by mechanisms such as methemoglobin formation. Nitrite is linked to the formation of carcinogenic *N*-nitrosamines *via* reaction with amino species (Singh et al., 2019) and as such the monitoring of this chemical species is often required for regulatory reasons. The measurement of nitrate and nitrite has a myriad of analytical options available (Dutt and Davis, 2002; Moorcroft et al., 2001; Singh et al., 2019; Wang et al., 2017). TE analysis is typically focused on the conversion of nitrates to nitrite by cadmium reduction, followed by quantitation using diazotised sulphanilamide and *N*-(1-naphthyl)-ethylenediamine dihydrochloride to form an azo dye complex that can be measured by colorimetric techniques. The sensitivity of this technique is suitable for TE analysis, without the need for expensive instrumentation or lengthy sample pre-concentration (American Public Health Association et al., 2017).

Table 2 Common analyses performed on industrial TE. Derived from Standard methods for the examination of water and wastewater analysis (American Public Health Association et al., 2017)

Target	Abbrev-iation	APHA	Method type	Reaction chemistry	Interferences	Measurement details
Turbidity		2130	Nephelometric	Direct measurement of scattered light	Colour, large particles, air bubbles	Nephelometer, light scattering at 90 °
Solids	TS	2540	Total solids	Solids dried at 103 to 105 °C	Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, fats/oils/grease, HCO_3^-	Gravimetric
	TDS	2540	Total dissolved solids	Sampled filtered through glass filter. Dissolved solids dried at 180 °C	Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, fats/oils/ grease, HCO_3^-	Gravimetric
	TSS	2540	Total suspended solids	Sampled filtered through glass filter. Dissolved solids dried at 103 to 105 °C	Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, fats/oils/ grease, HCO_3^-	Gravimetric
Conduct-ivity	CD	2510	Conductivity measurement	Direct measurement of sample conductivity	Sorption and poisoning of electrode surface, temperature	Conductivity
Oxidation reduction potential	ORP	2580	Oxidation reduction potential	Potentiometric measurement of electron activity	Sorption and poisoning of electrode surface, pH	Potentiometric measurement of redox potential of the sample
Cyanide	CN^-	4500-CN^-	Titration	Reaction between $AgNO_3$ and CN^- under alkaline conditions	Oxidising agents, S^{2-}, fatty acids, CO_3^{2-}, turbidity, colour	Titration with silver nitrate using p-diethylaminobezalrhodanine
			Colorimetric	Reaction between CN^- and chloramine-T to form CNCl, followed by reaction with pyridine-barbituric acid	Oxidising agents, S^{2-}, fatty acids, CO_3^{2-}, turbidity, colour	Spectroscopic (578 nm)

			Ion selective electrode	Direct measurement of CN^- by ion selective electrode	Oxidising agents, S^{2-}, fatty acids, CO_3^{2-}, turbidity, colour	Potentiometric
Chlorine	Cl	4500-Cl	Iodometric	Cl reaction with I^-	Mn and oxidising agents, S_2^-, NO_2^-, Fe	Titration with sodium thiosulfate with starch indicator
			Amperometry	Measurement of free, combined and total Cl by reaction with phenylarsine oxide	NCl_3, ClO_2, free halogens, Cu, Ag, NH_3	Titration, amperometry cell
			DPD ferrous titrimetric	Free Cl reacts with *N,N*-diethyl-p-phenylenediamine (DPD), addition of iodide catalyses the reaction of monochloramine and dichloramine	Mn and oxidising agents, CrO_4^{2-}, Cu, S_2^-, NO_2^-, Fe, Br, I	Titration with ferrous ammonium sulphate (FAS)
			DPD Colorimetric	Free Cl reacts with N,N-diethyl-p-phenylenediamine (DPD), addition of iodide catalyses the reaction of monochloramine and dichloramine	Colour and turbidity, CrO_4^{2-}	Spectroscopic (515 nm)
			Singaldazine	Singaldazine is oxidised by free Cl	Strong oxidising agents: I, Br, O_3	Spectroscopic (530 nm)
			Iodometric electrode	Reaction between I^- and Cl under acidic conditions	Oxidising agents: Mn, IO_3^-, Br, Cu^{2+}, Ag^+ and Hg^+ ions	Potentiometric, Iodide ion selective electrode
Chloride	Cl-	4500-Cl$^-$	Argentometric	Precipitation of Cl$^-$ with $AgNO_3$	Halides, S_2^-, $S_2O_3^{2-}$, SO_{32-}, PO_4^{3-}, Fe	Titration, potassium chromate indicator
			Mercuric nitrate	Reaction between mercuric nitrate ($Hg(NO_3)_2$) with chloride	Br^-, I^-. Chromate, ferric and sulphite ions	Titration, indicator diphenylcarbazone

			Potentiometric	Titration of Cl^- with $AgNO_3$	Bromide and iodide. Ferricyanide, chromate, dichromate	Potentiometric, glass and silver/silver chloride electrode
pH	pH	4500-H+	Electrometric	Direct measurement of H^+ activity	Sodium (pH > 10)	Potentiometric, pH electrode
Total Nitrogen	TN	4500-N	UV/Persulfate oxidation	Oxidation of N containing species to NO_3^- followed by reduction to nitrite using cadmium	Chlorine, hydrolysis at high pH, volatile loss	Spectroscopic (540 nm)
			High temperature persulfate oxidation	Oxidation of N containing species to NO_3^- followed by reduction to nitrite using cadmium	Chlorine, hydrolysis at high pH, volatile loss	Spectroscopic (540 nm)
Organic (Kjeldahl) nitrogen	TKN	4500-N Org	Kjeldahl method	H_2SO_4, K_2SO_4, and $CuSO_4$ catalyst react with amino nitrogen groups to form NH_3	NO_3^-, inorganic salts/solids, organic mater	Measurement via NH_3 measurement techniques.
Total Phosphorous	TP	4500-P	Sample preparation	Acid assisted hydrolysis. $HClO_4$; H_2SO_4/HNO_3; persulphate digestion	Dependent on measurement technique	Phosphate measurement (C/D/E).
Phosphate	PO_4^{3-}		Vanado molybdophosphoric acid	$(NH_4)_2MoO_4$ reaction to form $(NH_4)_3PMo_{12}O_{40}$, which subsequently reacts with V	SiO_2, AsO_4^{3-}, F^-, Th, Bi, S_2^-, $S_2O_3^{2-}$, SCN^-, MnO_4^{2-}, Cl^-	Spectroscopic measurement of vanado-molybdophosphoric acid (470 nm)
			Stannous chloride	Ammonium molybdate reaction to form molybdo-phosphoric acid, this complex is reduced by stannous chloride	SiO_2, AsO_4^{3-}, F^-, Th, Bi, S_2^-, $S_2O_3^{2-}$, SCN^-, MnO_4^{2-}, Cl^-	Spectroscopic measurement (690/650 nm)
			Ascorbic acid	Ammonium molybdate and Potassium antimonyl tartrate	AsO_4^{3-}, Cr(VI), NO_2^-	Spectroscopic measurement (880 nm)

					react with orthophosphate to form phosphomolybdic acid, this complex is reduced by ascorbic acid		
Nitrate	NO_3^-	4500-NO3	UV-spectro photometry	Direct measurement of NO_3^-	Organic matter	Spectroscopic measurement (220 nm)
			Ion selective electrode	Direct measurement of NO_3^-	Cl^-, HCO_3^-, NO_2^-, CN^-, S_2^-, Br^-, I^-, ClO_3^-, ClO_4^-	Ion selective electrode
			Colorimetric	Cadmium reduction of nitrate to nitrite followed by azo dye method for nitrite	Particulates, Fe, Cu, Cl2, fats/oils/grease	Spectroscopic measurement (543 nm)
Nitrite	NO_2^-	4500-NO2	Colorimetric	Azo dye complex formed between NO_2^-, diazotized sulfanilamide and N-(1-naphthyl)-ethylenediamine dihydrochloride	Sb^{3+}, Au^{3+}, Bi^{3+}, Fe^{3+}, Pb^{2+}, Hg^{2+}, Ag^{3+}, $PtCl_6^{2-}$, VO_3^{2-}, turbidity	Spectroscopic measurement (543 nm)
Ammonia	NH_3	4500-NH3	Titrimetric	Sample buffered to pH 9.5 and ammonia distilled into boric acid prior to titration	Sample distillation step required	Titration against H_2SO_4 with methyl red/methylene blue
			Ion selective electrode	Glass permeable electrode	Amines, Hg, Ag	Direct measurement via ion selective electrode
			Phenate	Sample buffered to pH 9.5 and ammonia distilled into boric acid prior to titration. indophenol complex formed from phenol and sodium nitroprusside	Sample distillation step required, Mg, Ca, turbidity, H_2S	Spectroscopic measurement (640 nm)
Dissolved oxygen	DO	4500-O	Iodometric method	Dissolved oxygen reacts with manganous hydroxide,	NO_2^-, Fe, particulates	Iodine formed can be measured via

				followed by reaction with Iodine in the presence of acid to yield Iodine		spectrophotometric, titrimetric, electrometric, potentiometric or dead-stop methods
			Membrane	Direct measurement of oxygen in situ	Salt	Polarographic or galvanic membrane electrode
Sulphide	S^{2-}	4500-S^{2-}	Methylene blue method	Reaction of sulphide with ferric chloride and dimethyl-*p*-phenylenediamine to produce methylene blue	Thiosulphate, ferrocyanide, Hg, Cd, Cu	Spectroscopic measurement (664 nm)
			Iodometric method		Reducing substances: thiosulphate, sulphite, organic compounds, Hg, Cd, Cu	Back titration of iodine with $Na_2S_2O_3$
			Ion selective electrode	Direct measurement of S_2^-	Humic compounds, oxidation	Silver/sulphide electrode
Sulphate	SO_4^{2-}	4500-SO_4^{2-}	Gravimetric	Precipitation of sulphate with HCl and $BaCl_2$	Particulates, NO_3^-, SO_3^{2-}, silicate, alkali metal sulphates, chromium, iron, barium chloride, barium nitrate	Gravimetric measurement of residue
			Turbidimetric	SO_4^{2-} is precipitated with $BaCl_2$ in the presence of acetic acid.	Colour or suspended matter, silica	Turbidimetric measurement with spectrometer (420 nm)
			Methylthymol blue	Precipitation of SO_4^{2-} with HCl and BaCl2, followed by reaction with methylthymol blue	Cations, molybdenum	Spectroscopic measurement (460 nm)
	COD	5220	Open reflux	Potassium dichromate ($K_2Cr_2O_7$) oxidation	Cl^- and halides, NO_2^-	Back titration with ferrous ammonium sulphate

Chemical oxygen demand			Closed reflux	Potassium dichromate $(K_2Cr_2O_7)$ oxidation	Cl^- and halides, NO_2^-	Back titration with ferrous ammonium sulphate
			Colorimetric	Potassium dichromate $(K_2Cr_2O_7)$ oxidation	Cl^- and halides, NO_2^-, particulates, light absorbing species	Spectroscopic measurement (420 or 600 nm)
Total Organic Carbon	TOC	5310	High temperature combustion	Catalytic degradation with CoO, Pt group metals or $BaCrO_4$	Inorganic carbon	Coulometric titration or infrared spectroscopy
			Persulfate	Temperature or UV assisted persulfate oxidation	Inorganic carbon	Coulometric titration or infrared spectroscopy
Biochemical Oxygen Demand	BOD	5210	5 day BOD test	Dissolved oxygen sensor	Nitrification reactions	Dissolved oxygen measurement at before and after a 5 day incubation period
Fats, oils and grease	FOG	5520	Partition-gravimetric	Solvent extraction with *n*-hexane or 80:20 *n*-hexane/methyl-*t*-butyl ether	Non-specific technique, Low pointing point compounds evaporate (<85 °C)	Gravimetric, residual mass after extraction solvent evaporation.
			Partition-infrared	Solvent extraction with CCl_3CF_3	Non-specific technique	Infrared spectroscopy (2930 cm^{-1})
			Hydrocarbons	Solvent extraction followed by absorption of polar compounds on silica gel, elution of hydrocarbons	Non-specific technique	Gravimetric or infrared spectroscopy (2930 cm^{-1})

In terms of phosphorous analysis, orthophosphate is the primary form that is found in TEs and domestic wastewater, along with waste and natural waters. As a result, analytical methods are focused on quantifying the range of phosphate fractions including total phosphorus (TP), which is derived from digestion of an unfiltered sample; total reactive phosphate (TRP) which is derived from analysis of an unfiltered undigested sample; and there are similar filtered equivalents of these measurements (Worsfold *et al.*, 2016). TP and TRP are important parameters for TE monitoring since phosphate is often a growth limiting nutrient in nature that can cause substantial negative impacts on biota due to eutrophication of water bodies (Maier et al., 2009; Withers et al., 2014). Detection of phosphates is achieved primarily by colourimetry using the molybdenum blue reaction with detection limits that are relevant to both TE and natural water body analysis (McKelvie et al., 1995; Nagul et al., 2015).

The most widely measured parameter of TE is hydrogen activity or pH due to the importance of this parameter relating to effluent processing and release conditions. Typically TE licenses specify acceptable ranges of pH 6 to 10 for release to sewers for the purposes of maintaining sewer integrity. Furthermore, industrial operations often monitor pH values for production reasons and variation outside desired set points can adversely affect product production and plant operation. pH measurements are primarily achieved using the pH ion selective electrode due to its ease of use and minimal interferences, other than high levels of salinity. The main disadvantages of conventional pH electrodes are the frequent calibration requirements to correct for response drift, electrode fragility and cost. There are a range of low-cost pH sensors in development however the glass-type electrode is still the most used approach due its convenience and accuracy.

Metals are another important group of inorganic species due to the potential toxicities of these species to humans and aquatic organisms (Jaishankar et al., 2014; Kavcar et al., 2009). Examples of priority heavy metals that are monitored for environmental release include: vanadium, chromium, cobalt, nickel, copper, zinc, arsenic, selenium, molybdenum, cadmium, tin, antimony, barium and lead (Jones et al., 2017). The techniques for metals analysis typically focus on more advanced instrument approaches like flame atomic absorption spectroscopy and inductively coupled plasma spectroscopy due to the low levels at which these species display toxicity. The monitoring of these metallic species can also be achieved using a range of ion selective electrode technologies (Zuliani and Diamond, 2012).

Sensors and process monitoring of TE

Grab, composite and passive sampling techniques introduce lag times between sample collection and measurement that lead to the collection of retrospective information about the composition of

TE. Automated samplers combined with chemical analysers such as flow or sequential injection systems (Miró and Frenzel, 2004) have been developed to enable the timely analysis of a range of inorganic species including nutrients, metals and organic species (O'Flynn et al., 2010). Flow injection analysers provide convenient means of introducing samples to flow through detectors, performing reaction chemistry for sample preparation or detection purposes. Separation techniques such as ion chromatography (IC) (Michalski, 2018), capillary electrophoresis platforms (Gaudry et al., 2013; Pham et al., 2014) can also provide capabilities and sequential detection of a range of cationic or anionic species that are relevant to TE, with reasonably fast cycle times although costly specialised instrumentation is required. To overcome this limitation, a range of sensor technologies have been developed to measure physical and chemical parameters in real time that are applicable to TE analysis (Kara et al., 2016). Some important examples of physical sensors include volumetric flow rate monitors, temperature, conductivity, dissolved oxygen, oxidation reduction potential and turbidity, some of which are already consistently utilised in industry (Kara et al., 2016; O'Flynn et al., 2010). Sensors have capacity to provide real time monitoring capabilities that could be invaluable for maintaining control over the properties of TE at the time of release (Zhuiykov, 2012).

Parameters such as DO and TN can exhibit substantial periodic variations even in natural environments (Hazelton, 1998) and industrial operations (Hauser et al., 2019) making high time resolution or real time measurement of target parameters potentially of interest. As an example, Figure 2 shows monthly COD values reported by a biopharmachem company showing concentrations ranging from 80 to 1600 mg/L with an average value of 380 mg/L (standard deviation 450 mg/L). The loadings of COD released by this site varied over 3 orders of magnitude across the year and the average yearly value does not adequately capture the short-term variation around the months of April and May, which were substantially greater than levels reported for the rest of the year. This demonstrates the value of real time monitoring compared to lower time resolution measurements (grab/composite sampling), as has been identified in other environmental applications such as monitoring WWTP effluent, marine, costal and river water sites (Blaen et al., 2016; Bowes et al., 2009).
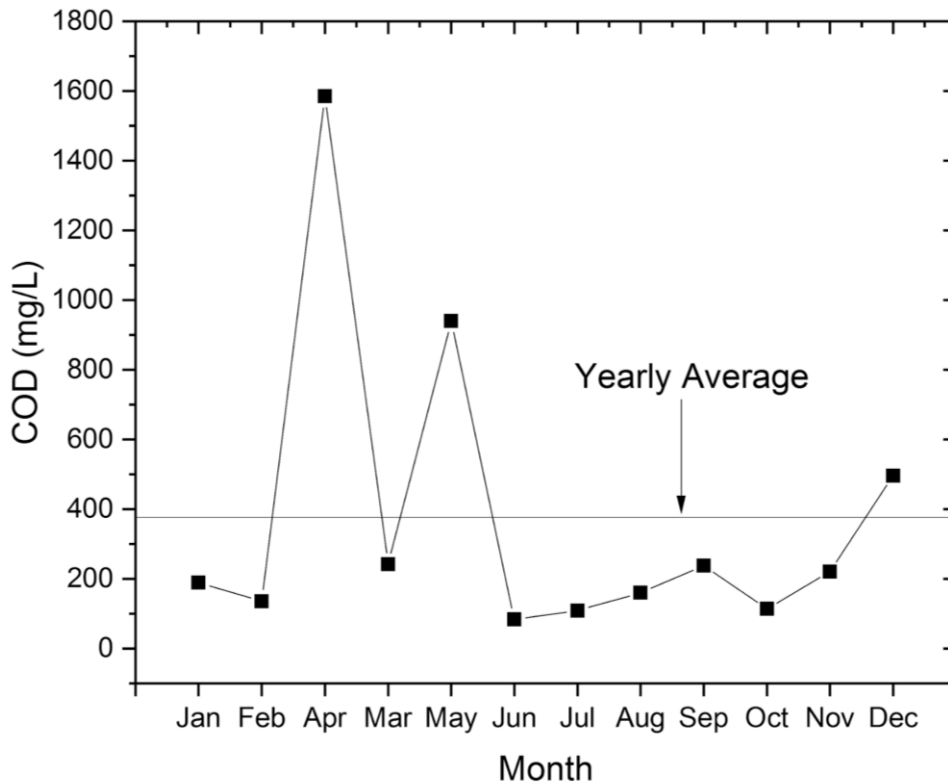
Figure 2 Example data of the monthly variation in COD concentrations reported for a biopharmachem company

An additional bottleneck of analysis is the time required for the analytical measurement itself, for example most metals and nutrient analyses require digestion reactions prior to the measurement of these parameters, which vastly reduces analytical throughput. Similarly, chromatographic techniques are limited by the duration required to complete a separation. The constraints of sampling and analytical measurement techniques often lead to the collection of retrospective information on the composition of TE, rather than directly providing information in real time, which would be valuable for the rapid determination of TE composition.

Real time monitoring of TE attempts to overcome this throughput limitation, moving from a reactive control model, to a scheme where the frequency of data collection is rapid enough to allow the prediction and control of TE parameters. Thresholds for parameters can be set to enable action to be taken ahead of time to prevent the release of effluent that is not of the desired standard. There are a range of sensor technologies available that provide physical and chemical measurements as summarised in Table 3.

Table 3 Sensors utilised for monitoring TE parameters

Sensors	Licensed parameter	Surrogate potential
Ammonia/Ammonium	Yes	TN, nitrates, nitrite
Cadmium	Yes	
Calcium	Yes	Water hardness
Chloride	Yes	Salinity
Conductivity	No	Organic, inorganic and metallic species. Suspended solids.
Copper	Yes	
Cyanide	Yes	
Dissolved oxygen	No	BOD, COD
Fluoride	Yes	
Iodide	Yes	
Lead	Yes	
Near Infrared	No	COD, TOC, organics, inorganics, metals, fats oils greases
Nitrate	Yes	TN, ammonia, nitrite
Oils, hydrocarbons	Yes	Fats oils greases,
Oxidation reduction potential	No	Organic, inorganic and metallic species.
pH	Yes	Conductivity, ORP, acidity, alkalinity
Potassium	Yes	
Silver	Yes	
Sodium	Yes	Salinity
Sulphide	Yes	Sulphur containing species, sulphate
Temperature	Yes	Septicity
Turbidity	No	Suspended solids, COD, organics, inorganics
UV-Vis	No	COD, TOC, organics, inorganics, metals, fats oils greases
Volumetric flow	Yes	Mass loadings

Some important examples of physical sensors include volumetric flow rate monitors, temperature, conductivity, DO, ORP and turbidity. Volumetric flow rate sensor requirements are incorporated into TE licences for the purposes of determining chemical and particulate emissions by industrial sites. Conductivity sensors measure the ability of a solution to carry an electrical current which is linked to the ionic strength of the solution. Charged organic, inorganic and metallic species within a sample contribute to the bulk conductivity of TE samples and the variation in conductivity parameters can be invaluable in detecting changes in TE composition when correlated with components of the sample (Blaen et al., 2016; Hauser et al., 2019; J. Yang et al., 2009). Dissolved

oxygen sensors measure the levels of oxygen species either using galvanic or optical properties of water samples which is linked to the BOD and COD parameters in TE as oxygen content impacts the oxidation of TE components (Y. Xie et al., 2016). Oxidation reduction potential (ORP) provides information on the capacity of a sample to oxidise or reduce chemical species within TE, which can be useful for determining the reactivity of a waste stream and efficiency of effluent treatment measures in place in WWTPs or industrial sites (Dries, 2016). Both ORP and conductivity are simple measures to perform however the data obtained is a composite of the redox behaviour of species present in the system, the pH and ionic strength (Claros et al., 2012).

Turbidity measurements can be rapidly performed using laboratory nephelometers, or turbidity sensors, in real time providing a bulk measure of particulates in a sample; however, such online measurements do not distinguish between TSS and TDS without the application of filtration. Furthermore, particle settling complicates sampling and use of turbidity, and the placement location of turbidity sensors can significantly impact the measurements obtained, while solids measurements are not as sensitive to these features providing that a representative TE sample is obtained. The colour and size of particles substantially impacts the scattering obtained during turbidity measurements and must be considered. The simplicity of the TSS and TDS measurements eliminate concerns with light absorbance in nephelometers, however the time required to evaporate water from these samples results in a low analytical throughput which is not amenable to online analysis. Conductivity measurements provide another useful physical parameter that is broadly indicative of the levels of ionic species within a sample and when combined with other parameters such as pH, ORP it can be used to model the performance of complicated systems to allow control over TE properties (Capodaglio, 2017; Jeffrey Yang et al., 2009).

Out of the chemical sensors, the most prevalent is undoubtedly the pH electrode, which measures the activity of hydrogen ions in a sample. This parameter impacts the ionisation state of all components of a sample and affects the reactivity of all species in solution. For this reason pH values are typically measured in real time with effluent output levels dictated by environmental regulators. Other chemical sensors include the related ion selective electrodes (ISEs) which have capabilities for the measurement of a wide variety of licensed parameters such as fluoride, chloride, bromide, iodide, nitrates, ammonia, cyanide, thiocyanate, lithium, sodium, calcium, potassium, copper, silver, lead and cadmium (Hu et al., 2016; Zuliani and Diamond, 2012). ISEs provide information about the activity or concentration of soluble metallic species in environmental samples such as those derived from TE (Crespo, 2017). ISE technologies have capacity for providing low cost sensing environmentally relevant cations and anions and these sensors can

easily be integrated with wired or wireless sensor networks, to enable the selective quantification of ions across extended dynamic ranges (Zuliani and Diamond, 2012), many of the target ions are included in TE licences. The primary limitations of ion selective electrodes include (i) electrode fouling from sample matrix components, (ii) electrode drift in response to constant exposure to sample matrix, (iii) electrode dissolution, (iv) electrode carryover due to slow mass transfer kinetics, and (v) electrode response instability resulting from passivation of the ISE in response to matrix components (De Marco et al., 2007). The equilibration of ISE with sample matrices provides stabilisation against electrode drift and dissolution. The effects of fouling, carryover and signal instability require careful consideration. Optimisation or operational protocols can be used to clean and calibrate electrode surfaces overtime, to reduce error associated with fouling. Flow injection analysers and continuous flow analysers provide some capacity to improve and stabilise the signals of ISEs by utilising shearing flows and surface cleaning strategies (De Marco et al., 2007). While ISEs are not able to access the level of heavy metals bound in solid particulates, the levels of these species in the associated TE are potentially linked via dissociation constants. Acidification of samples is one strategy available to analysts to dissolve and access the metallic components bound to solid particulates and such digestions are commonly performed during total metals analysis via techniques such as inductively coupled plasma atomic emission spectroscopy/mass spectrometry or atomic absorption spectroscopy.

Nitrate, nitrite and ammonia sensing has been achieved with a selection of ISE technology that has been successfully deployed in WWTP and environmental applications for regulatory and process control applications (Wang et al., 2017; Y. Xie et al., 2016). Phosphate monitoring is of particular interest due to the value of this target for recovery and its consistent inclusion as a regulated parameter in TE licences. Receiving waters in Ireland are sensitive to elevated nutrient levels from diffuse or point sources, therefore monitoring and regulation of these parameters is critical. Development of a phosphate sensor is confounded by molecules of similar size and activity such as the sulphate anion (Warwick et al., 2014, 2013). Phosphate is also strongly hydrated due to the oxygen molecules surrounding the phosphorous core which limits the selectivity of existing phosphate sensors, necessitating the application of colorimetric (Nagul et al., 2015), electrochemical or fluorescence emission spectroscopy (Warwick et al., 2014, 2013; Worsfold et al., 2016). Electrochemical solid-state sensors (based on metal oxides) are low cost, potentially disposable, easy to manufacture with a range of selectivity's and appropriate sensitivities required for TE analysis (Hu et al., 2016; Zhuiykov, 2012).

Spectroscopic sensors have also been demonstrated as highly valuable for tracking TE parameters using UV-vis spectrophotometry (Baurès et al., 2007; Singh et al., 2019) and

fluorescence (Carstea et al., 2016; Henderson et al., 2009; Reynolds, 2002). Instream monitoring of waste water quality (Capodaglio, 2017) can be performed in industrial and WWTP facilities for process monitoring of waste water, however it is not ubiquitously utilised due to its associated costs. Spectroscopic techniques are able to detect and quantify organic components such as the species that contribute towards the COD parameter that is commonly reported as a measure of organic loading (Ye et al., 2018). Similarly, there are a range of BOD measurement techniques that are achieved via the use of spectroscopic/galvanic dissolved oxygen sensors combined with other UV-vis measurements that inform on the otherwise slow to measure BOD parameter (Altenburger et al., 2015; Jouanneau et al., 2014; Reshetilov et al., 2013). UV-Vis and infrared spectroscopy is useful for monitoring hydrocarbons and chlorinated species in TE particularly in the biopharmaceutical and waste management sectors as these compounds often comprise these waste streams (Melendez-Pastor et al., 2013; Morisset et al., 2018). Such approaches are valuable for performing real time analysis as an alternative to chemical analysis techniques and similar capabilities have been demonstrated for TSS, nitrate, nitrite, TN, ammonia, phosphate and TP (Dutt and Davis, 2002; Singh et al., 2019; Thomas et al., 1997; Y. Xie et al., 2016).

TE streams

The components and loadings of these components in TE varies between different industrial sites and sectors. However, for each site there are two main effluent properties that must be considered, the concentrations of components being released to sewer and mass loadings being emitted which can be obtained by integrating the concentrations of each component with flow measurements. Industrial licences specify both maximum allowable concentrations for licensed parameters along with maximum mass loadings allowed over periods of time. Dilution of effluent streams with water can provide capacity to reduce peak concentrations of licensed species, however dilution does not assist with reducing loadings emitted, can result in exceedances in daily hydraulic discharge limits; and has the additional costs due to the fact that industry are typically charged for sewer emissions on volumetric unit basis. Some industrial sites have multiple water consuming processes, and these effluent streams may be isolated from one another for treatment and disposal reasons. For example, a site may utilise water as a coolant, an extractive solvent (*e.g.* steam distillation), for cleaning purposes, or as a solvent for synthetic procedures and the properties of the wastewater from each of these effluent streams will be completely different (Alayu and Yirgu, 2018; Deegan et al., 2011; Gadipelly et al., 2014). Water used as a coolant or for steam distillation may have characteristically high temperature at release, however the steam distillation effluent stream may also contain considerable quantities of organic compounds. Dilution and chemical treatment of effluent is often necessary to control parameters such as pH, temperature and the concentration of species within the TE prior to treatment or

release. Examples of the processes, parameters and monitoring strategies implemented in each of the selected TE streams is shown in Figure 3.
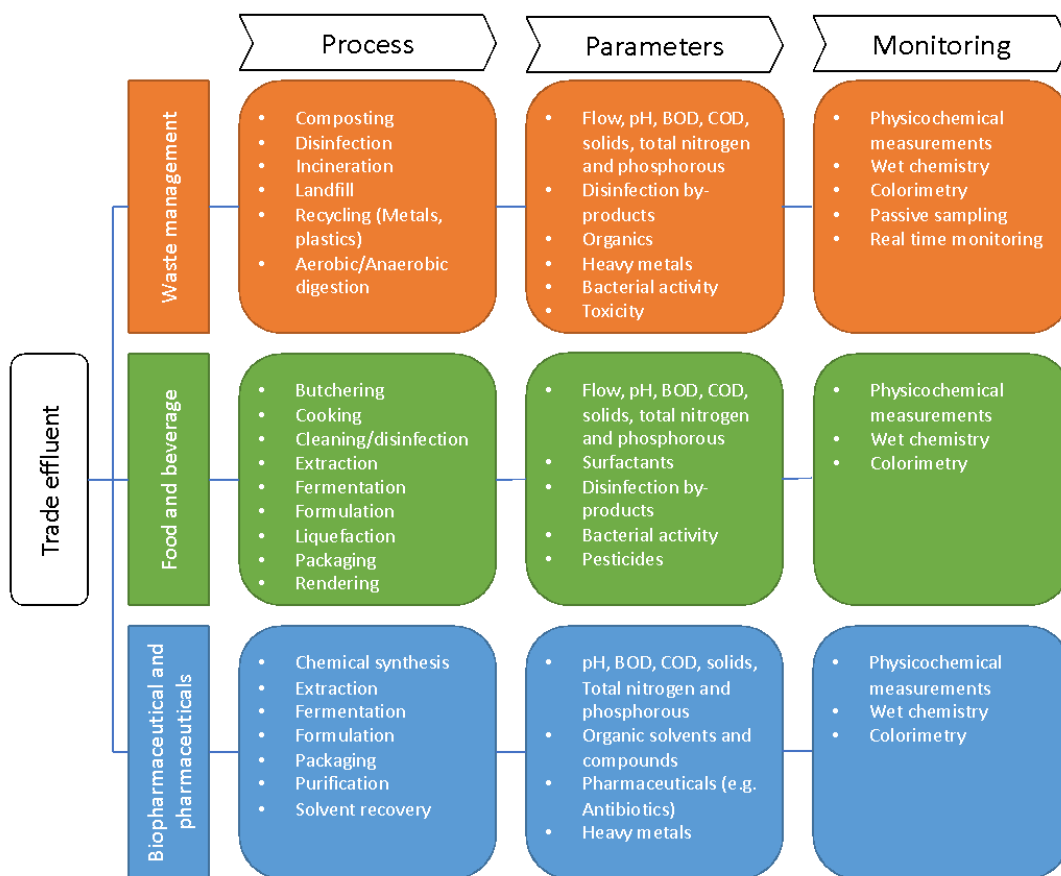
Figure 3 Flow diagram showing the TE streams for three industrial sectors, summarising typical processes, parameters of interest and common monitoring approaches

The complexity of wastewater necessitates the use of a diverse suite of analysis techniques ranging from simple physical measurements of flow and temperature, to sensors (*e.g.* pH, ORP) and chemical analysis techniques for organic, inorganic and metallic species.

Wastewater monitoring provides industry with valuable information about the status of on-site processes, for example the presence of particular compounds may suggest the deterioration of elements of industrial processes, for example an increase in suspended solids may reveal that a sedimentation or filtration step in the site process requires maintenance. Additionally, this information is valuable for maintaining regulatory compliance with TE licenses, which are designed to prevent damage being done to sewer or WWTP networks downstream from industrial sites. Figure 4 shows a summary of the most prevalent licensed parameters that are reported across three water consuming sectors focused on in this review. The focus on monitoring

parameters such as COD, BOD, TSS, TN, TP, sulphate, phosphate and ammonia parameters is due to their impact on sewer integrity and WWTP function. For example, nutrient parameters such as COD, BOD, TN, TP, phosphate and ammonia can contribute to the growth and proliferation of bacteria and septicity in the presence adequate effluent temperatures and retention times. High levels of particulates as measured by TSS can sediment in sewer and WWTP systems increasing the frequency of maintenance required for adequate operation (American Public Health Association et al., 2017). To evaluate the typical levels of licensed parameters in the three sectors of interest, 53 AER reports were collected (14 biopharmachem, 21 food/beverage and 18 waste management AERs) for a three-year period (including 2015, 2016, 2017). Similarly, literature review data was obtained from a range of sources covering matching company types and years for comparison purposes.
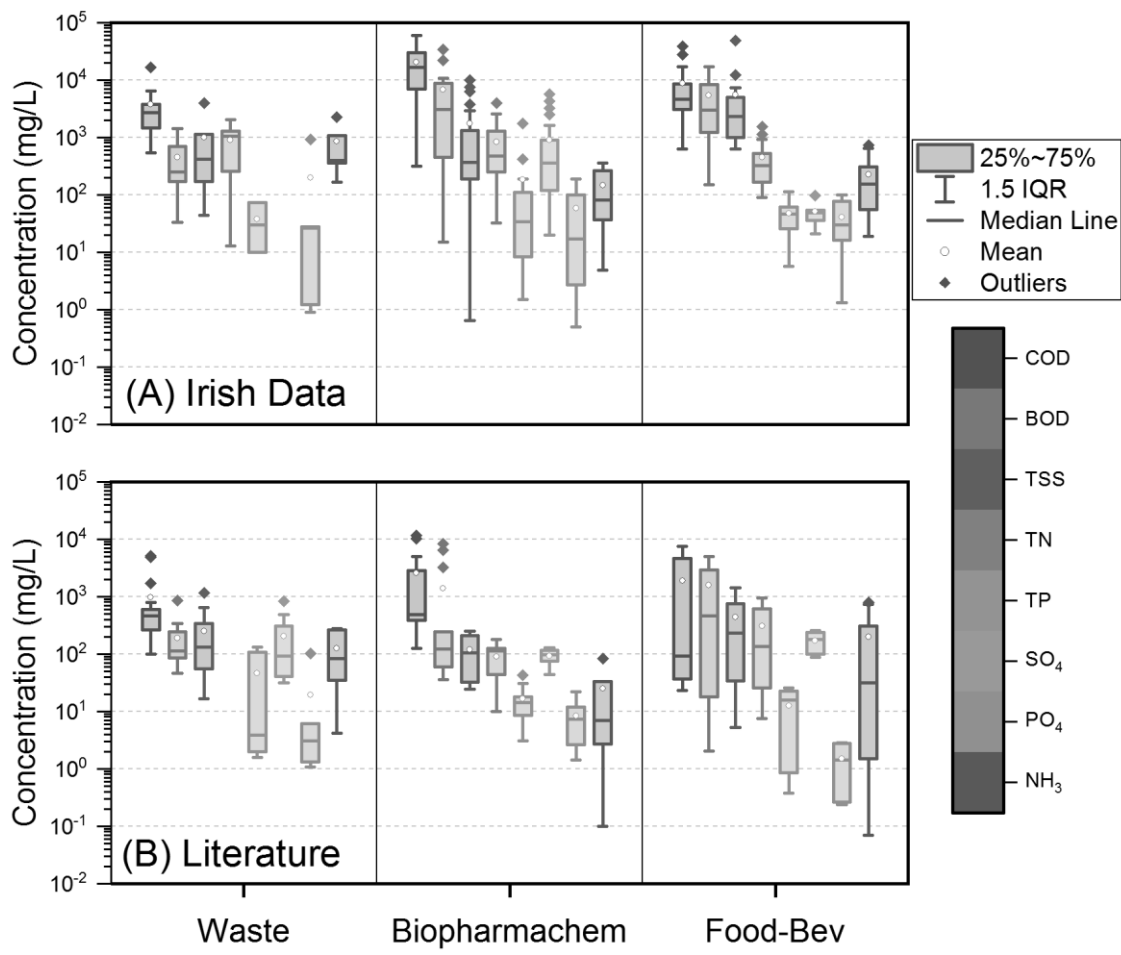
Figure 4 Comparison of the range of concentrations reported for eight parameters across the three designated TE sectors. (A) Shows concentration data derived from Irish AER's

from a representative selection of industrial companies with data obtained from the years 2015, 2016 and 2017. (B) shows average concentration data reported from international wastewater monitoring studies for the three sectors of interest

One of the most frequently reported chemical parameters in wastewater monitoring studies is pH (65% of AERs) which provides a measure of the acidity or alkalinity of TE streams. This is important for sewer release conditions, since excessively acidic or alkaline effluent can cause damage to sewer systems via corrosion or reaction with other TE released to the network. pH is often restricted to a window around neutral pH, and this is achieved by balancing the pH of effluent prior to release. Balancing is usually performed by the addition of sodium hydroxide to increase pH, or via the addition of inorganic acids (such as hydrochloric or sulphuric) to reduce pH to a desired level.
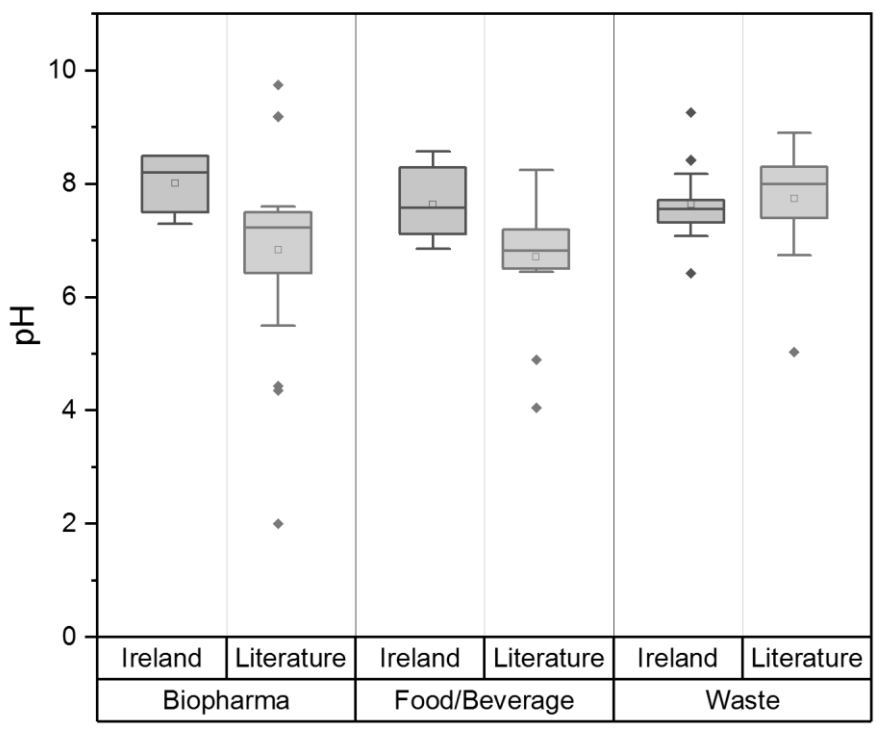
Figure 5 Comparison of pH values measured for TE across three sectors, comparing data derived from Irish AERs and a literature review of international data

In Ireland the pH of released TE was on average 7.7 ± 0.6 for all three categories, with similar group averages and distributions of values as shown by Figure 5. This narrow distribution of pH values are caused by the regulation of this parameter which has incentivised companies to adjust TE pH prior to release. TE released by Irish biopharmachem and food/beverage companies

appears to be a little more alkaline in pH compared to equivalent international values, however this likely reflects differences in regulated pH preferences of international companies rather than differences in the products made by companies in each scenario.

TSS was the most frequently reported parameter in Irish AERs (94 %) due to the general correlation this parameter has with mass loadings in TE. Figure 6 shows the distribution of TSS values for the Irish and international scenarios. It can immediately be seen that lower TSS values are reported in all three Irish sectors compared to international data, however of the three sectors the food/beverage group contributes higher levels of suspended solids that biopharmachem or waste management industry.
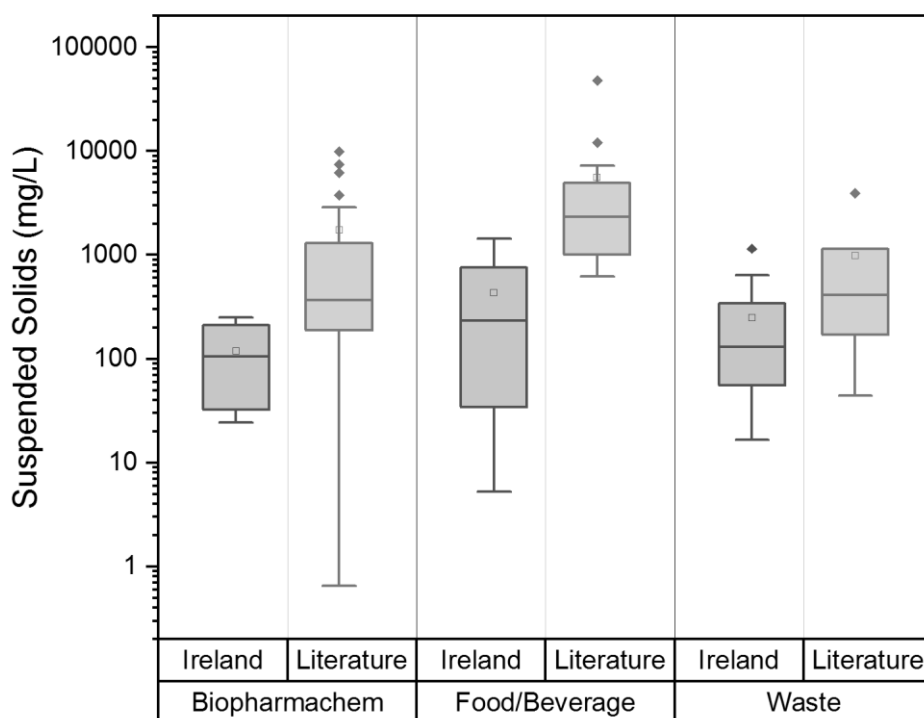
Figure 6 Comparison of total suspended solids values measured for TE across three sectors, comparing data derived from Irish AERs and a literature review of international data
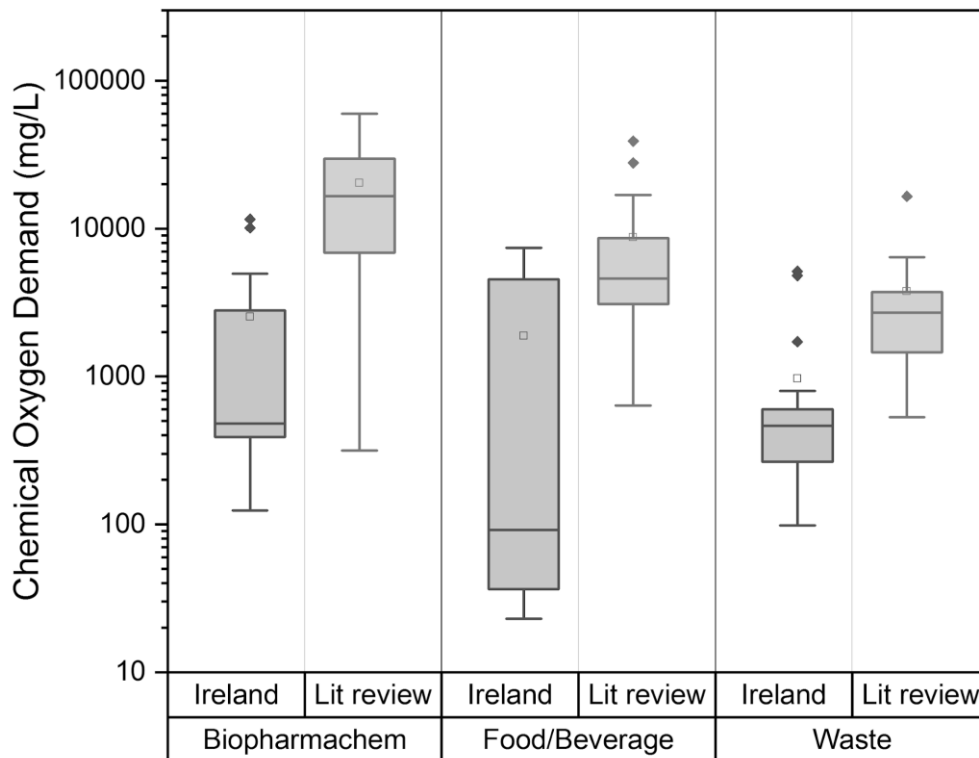
Figure 7 Comparison of COD values measured for TE across three sectors, comparing data derived from Irish AERs and a literature review of international data

COD levels (79 % of AERs) were similarly somewhat lower than literature review data although the range of values reported covered the same orders of magnitude. Of the three sectors, food/beverage has the greatest variation in reported COD values, which is caused by differences in company investment in treatment systems prior to TE release. Some companies incorporate dissolved air flotation systems or anaerobic/aerobic digestion reactors that provide capacity for reduction of COD and other parameters while others do not have this infrastructure. This also explains when international data reveals systematically higher levels of COD parameters, as some countries TE is not as stringently regulated, particularly in developing countries.
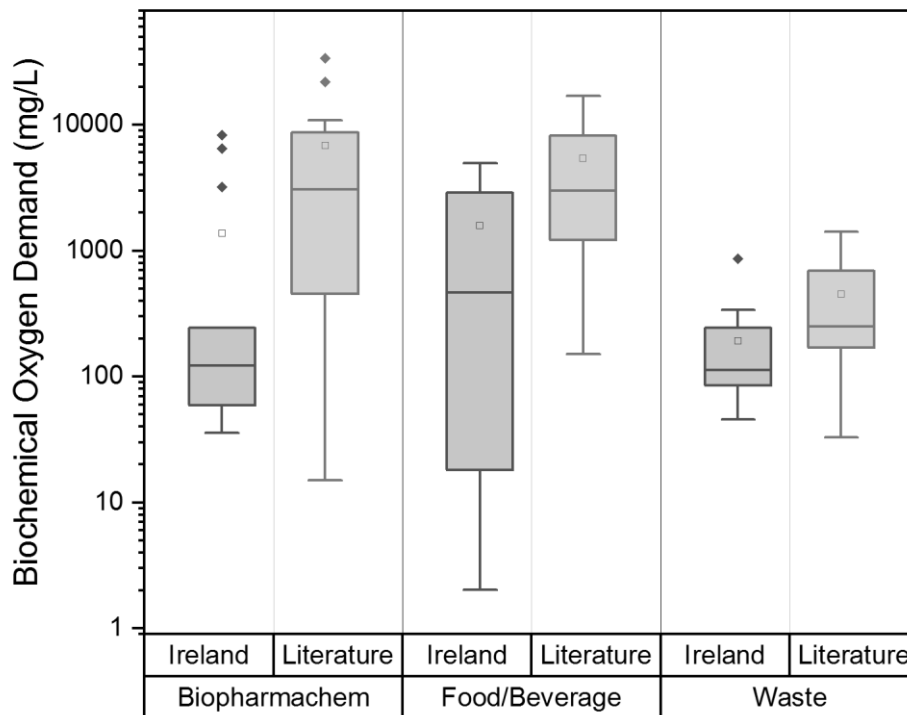
Figure 8 Comparison of BOD values measured for TE across three sectors, comparing data derived from Irish AERs and a literature review of international data

BOD is another consistently reported AER parameter (94 % of AERs) due to the unique information it provides regarding the biological activity of released wastewater. Food/beverage TE yielded the widest range of reported BOD values as shown in Figure 8, and Irish AER data was comparable to the international scenario across the three TE categories. The wide range of food/beverage TE BOD values is caused by the biologically derived nature of food and beverage products which can harbour and support the growth of biological species.

TN is the most consistently reported chemical parameter in the food/beverage sector compared to biopharmachem and waste management industries due to the substantial protein components of TE derived from these sectors. Similarly, biopharmachem industries also consistently report TN for cell-culture based drug production. The levels of TN in the Irish and international scenarios were similar. In the Irish waste management sector, the industry is more focused on ammonia levels resulting from degradation of organic material, explaining the lack of TN data obtained from AERs from this sector.
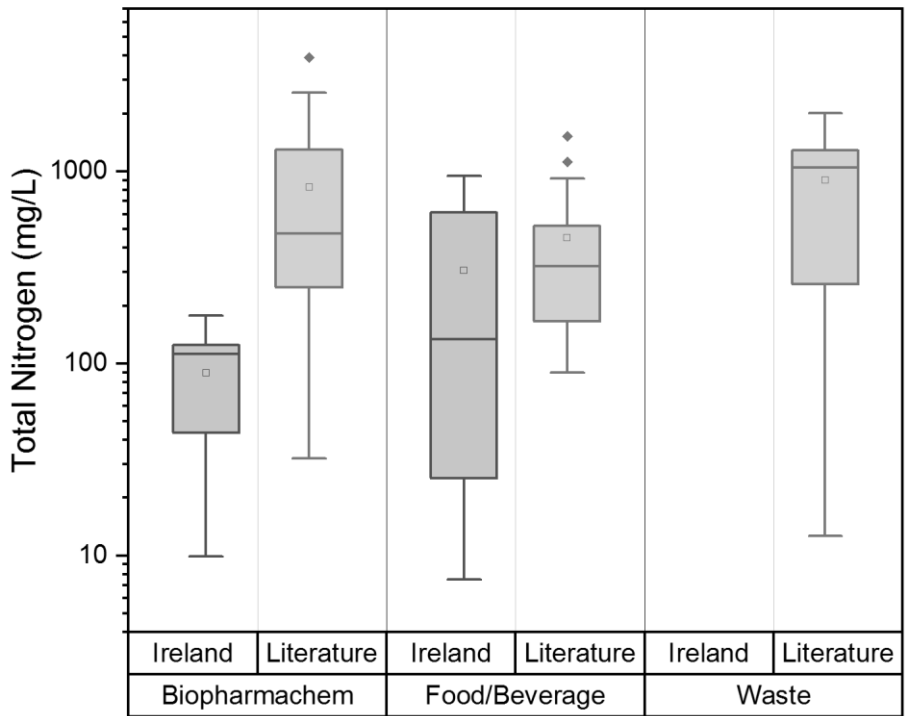
Figure 9 Comparison of TN values measured for TE across three sectors, comparing data derived from Irish AERs and a literature review of international data

Ammonia levels were included in 55% of Irish AERs, and this parameter is monitored due to the corrosive impact that this species can have on sewer systems in addition to its potential for contributing to odour, and increasing the operational costs associated with its removal downstream in WWTPs. Food/beverage and waste management sectors are shown in Figure 10 to contribute the largest loads of ammonia to TE due to the biodegradation of organic material that occurs in the waste typically produced or processed by these industries. Interestingly the levels of ammonia reported by Irish biopharmachem companies is somewhat lower than the other sectors and international data suggesting that the regulator requirements for this sector are more demanding that the other sectors. This point is worth considering from a regulations perspective for this sector – or elements of the sector.
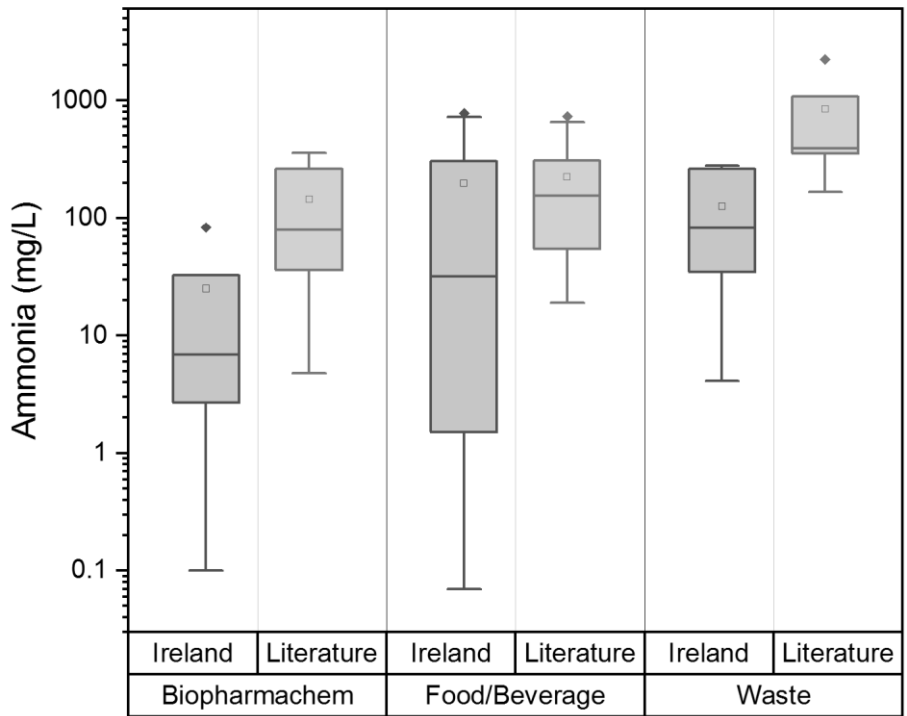
Figure 10 Comparison of ammonia values measured for TE across three sectors, comparing data derived from Irish AERs and a literature review of international data

TP (Figure 11) and orthophosphate (Figure 12) are important parameters that can contribute to the growth of bacterial and algal species. Phosphate is produced during the degradation of phosphorous containing TE, and phosphate in particular can be a commodity worth extracting for usage in fertiliser products (Peng et al., 2018; Song et al., 2018; Zhao et al., 2018).
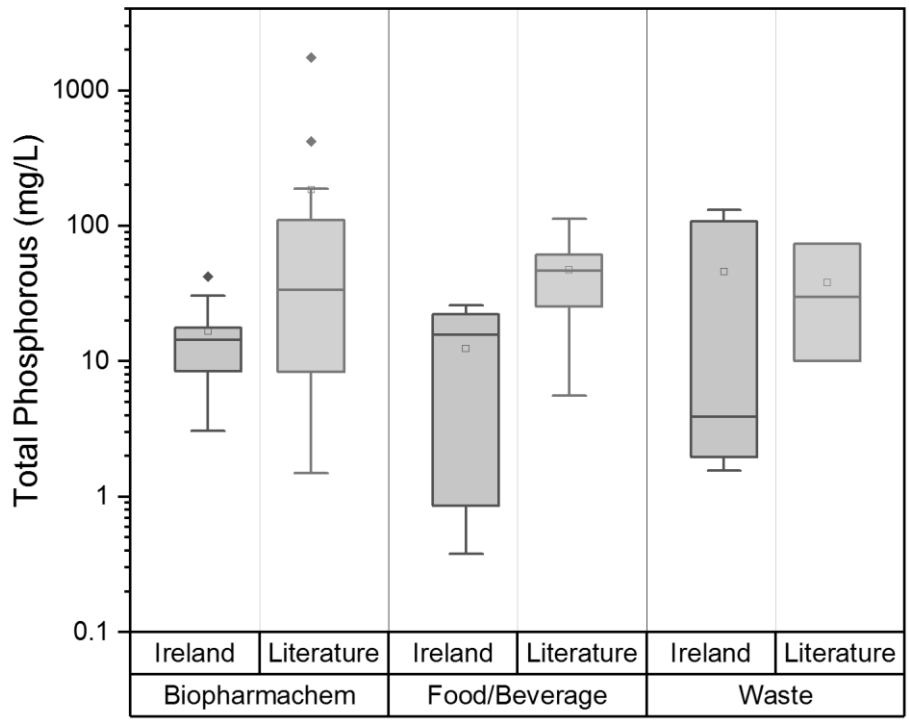
Figure 11 Comparison of TP values measured for TE across three sectors, comparing data derived from Irish AERs and a literature review of international data
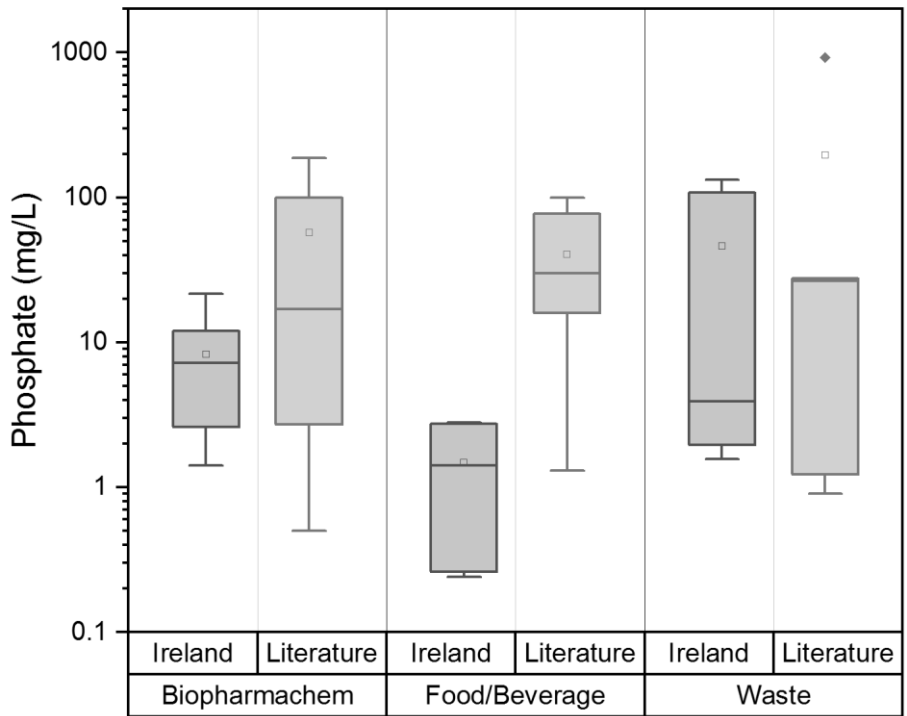
Figure 12 Comparison of phosphate (as orthophosphate) values measured for TE across three sectors, comparing data derived from Irish AERs and a literature review of international data

Sulphates, shown in Figure 13, are not typically a challenge for WWTP removal processes, however sulphates can affect sewer health if they are present at levels exceeding 1000 mg/L (American Public Health Association et al., 2017). These high concentrations can lead to formation of sulphides that contribute to septicity and odour in pipes. Additionally high levels of sulphate can form dilute sulphurous acid and contribute to corrosion of pipes, hence the necessity for monitoring of this parameter.
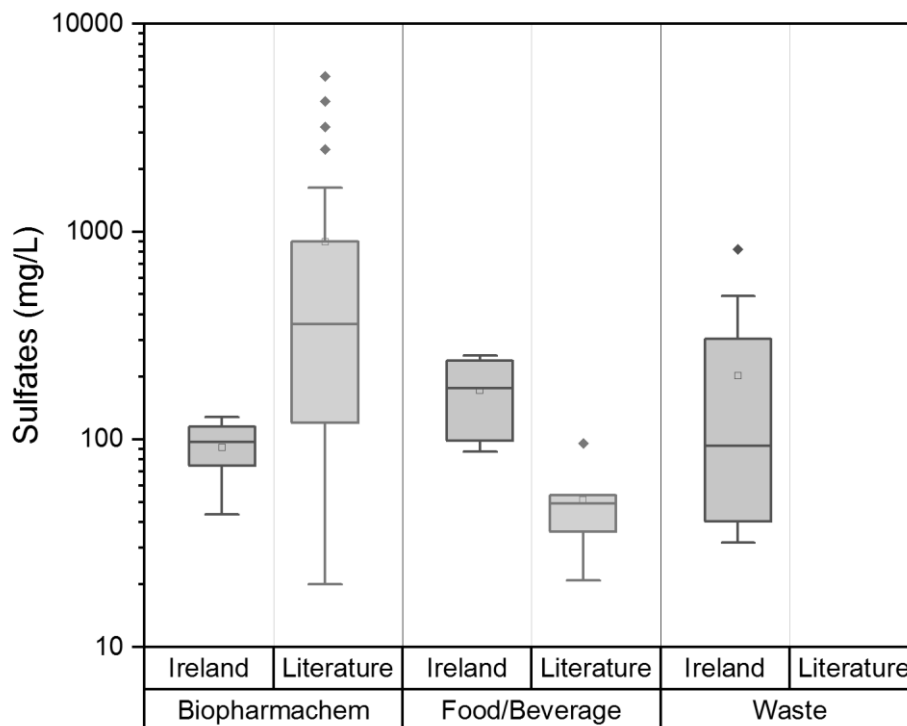
Figure 13 Comparison of sulphpate values measured for TE across three sectors, comparing data derived from Irish AERs and a literature review of international data

The following sections go into detail about other licensed components that are monitored in Irish waste water for the food/beverage, biopharmachem and waste management sectors. Additionally, each section includes information on other potential surrogates that may be present in these TE streams that could inform industry or regulators about TE quality.

Food and beverage

Some TEs generated by the meat (Kundu et al., 2013; Sunder and Satyanarayan, 2013), dairy (Demirel et al., 2005; Ince, 1998) and beverage industries (Kumar, 2015) have high concentrations of total solids, organic and inorganic nutrients due to the usage of water during food/beverage preparation (*e.g.* boiling, steaming and simmering), processing and cleaning (Alayu and Yirgu, 2018; Demirer et al., 2000). This use of water for food and beverage processing can cause substantial contributions to BOD due to the levels of organic compounds and microbial species that may be present in these TE streams (Alayu and Yirgu, 2018; Demirer et al., 2000). The biodegradable nature of contaminants derived from food processing activities result in a TE stream that is highly susceptible to aerobic and anaerobic processing either on site or at downstream WWTPs (Demirer et al., 2000). High temperature effluent release of biologically

derived waste can impact the microbial growth levels within sewers leading to septic conditions that produce odour and potentially cause system blockages and damage (American Public Health Association et al., 2017). As a result, the main parameters monitored in food/beverage waste are the primary nutrients parameters summarised in Table 4 below, along with ammonia, phosphate in addition to the soluble microbial products that are generated during biological degradation procedures such as sugars, and short and medium chain fatty acids (Barker and Stuckey, 1999).

Table 4 Summary of licensed parameters for the Irish AER data related to the food/beverage sector

Parameter	N total	Median	Mean	Standard Deviation	Minimum	Maximum
pH	9	7.58	7.64	0.65	6.86	8.57
Temperature	3	21.32	21.28	0.48	20.78	21.73
Volumetric flow (m³/day)	6	3709	3883	3600	584	7362
Annual water emission (kg)	12	2.0 E+07	5.0 E+08	7.0 E+08	6.0 E+09	2.0 E+08
COD (mg/L)	12	91.7	1882.7	2654.1	23.0	7411.1
BOD (mg/L)	21	466.4	1578.2	1703.5	2.0	4958.8
TSS (mg/L)	21	233.0	434.7	469.7	5.3	1435.9
TN (mg/L)	12	133.8	306.4	373.2	7.5	950.8
TP (mg/L)	15	15.7	12.4	10.4	0.4	25.8
Sulphate (mg/L)	6	176.9	172.2	73.4	87.6	253.7
FOG (mg/L)	18	4.7	18.4	27.5	1.5	104.6
Detergents (mg/L)	9	0.5	1.6	1.8	0.0	5.3
Phosphate (mg/L)	6	1.4	1.5	1.3	0.2	2.8
Ammonia (mg/L)	15	31.8	196.3	292.0	0.1	785.4
Copper (mg/L)	3	0.0	0.0	0.0	0.0	0.0
Chlorides (mg/L)	6	934.2	894.3	720.5	166.1	1598.6
Zinc (mg/L)	3	0.1	0.1	0.0	0.1	0.1
TOC (mg/L)	3	1527.8	1541.1	41.1	1508.3	1587.2
Total oxidised nitrogen (TON)	3	2.7	2.7	0.0	2.7	2.7
Total heavy metals (mg/L)	3	0.0	0.2	0.2	0.0	0.4

Slaughterhouse operations can contribute organic pollutants such as fat, oils, and tissue particulates along with the manure and urine associated with animal carcasses, in particular blood is a significant water soluble pollutant that yields very high COD levels (Bustillo-Lecompte and Mehrvar, 2015; Kundu et al., 2013). Effluent from the dairy industry contains organics and nutrients that are present in milk; including fats, sugars and proteins, in addition to additives used during dairy production such as flavourings and preservatives. Casein and whey protein are substantial components of milk that are by-products of cheese production; dairy effluent also contains modest amounts of lactose, lactic acid, citric acid, urea, uric acid, inorganic salts (sodium chloride, potassium chloride and calcium phosphate) that contributed to nutrient parameters COD levels in TE (Chatzipaschali et al., 2012). Dairy waste contains high levels of soluble protein in the form of organic nitrogen containing compounds. The recovery of lactose and whey proteins from dairy products is common due to the industrial value of these products as food products/supplements, binders or in fertilisers (Bustillo-Lecompte and Mehrvar, 2015; Chatzipaschali et al., 2012). Beverage preparation can involve a wide range of processes including fermentation during alcohol production, extraction for fruit juices and the formulation of artificial sodas (Valta et al., 2015). Processed food and beverage products can have high levels of additives such as salt, flavourings, colourings and other preservatives that contribute towards parameters found in TE (Ghosh Ray and Ghangrekar, 2018).
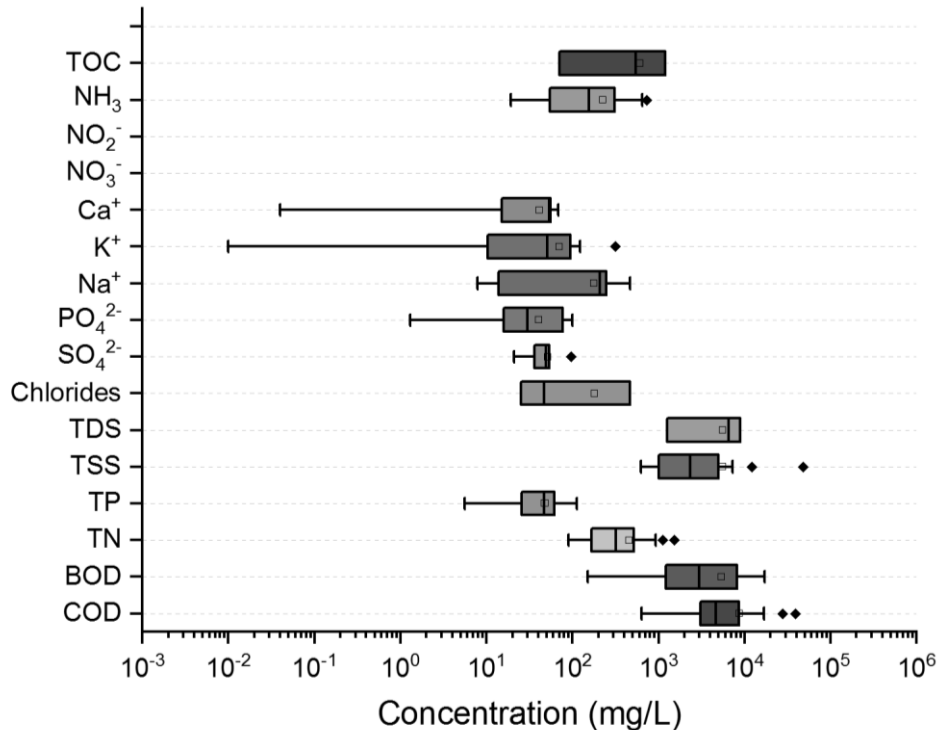
Figure 14 Comparison of the concentrations of licensed parameters reported in Irish AER data for the food/beverage industry

Food/beverage companies utilise a range of technologies to reduce the organic and nutrient loadings of their TE, including anaerobic, aerobic, dissolved air flotation and other membrane purification techniques (Alayu and Yirgu, 2018; Demirel et al., 2005; Mittal, 2004; Valta et al., 2015).

Biopharmachem industries

The contents of biopharmachem industry wastewater can be divided broadly into five types of processes including fermentation, extraction, chemical synthesis, product formulation and packaging (Ince et al., 2002; Shi et al., 2017). Whether a site is designed to produce small molecule drug products or large molecule biopharmaceuticals will vastly change the profile of the wastewater from a site (Gadipelly et al., 2014; Lefebvre et al., 2014; Rana et al., 2017). There are a number of technologies that are employed in industry to reduce the nutrient, organic and inorganic species released to sewer, however there is a strong focus on the minimisation of BOD, COD, chlorides and TN parameters which can be achieved *via* aerobic/anaerobic or membrane purification processing steps (Degirmentas, 2004; Ng et al., 2014; Rodríguez et al., 2005). Pharmaceutical companies are also regulated for heavy metals content in their discharged TE due to the use of these species during synthetic and purification procedures (Sharif et al., 2016). Heavy metals such as arsenic, cadmium, copper, lead, nickel and zinc have also been detected in pharmaceutical TE (Bielen et al., 2017), however the release of these species is restricted to sewer or transported to waste processing plants for recovery/removal.

Table 5 Summary of licensed parameters for the Irish AER data related to the biopharmachem sector

Parameter	N total	Median	Mean	Standard Deviation	Minimum	Maximum
pH	7	8.2	8.01	0.48	7.3	8.49
Temperature	7	22.90	20.59	6.63	11.25	29.00
Volumetric flow (m^3/day)	3	94.80	99.26	26.10	75.67	127.30
Annual water emission (kg)	14	3.E+07	2.E+08	2.E+08	3.E+06	5.E+08
COD (mg/L)	12	479.37	2539.17	4102.08	124.00	11560.85
BOD (mg/L)	14	121.99	1369.11	2701.57	35.92	8307.73
TSS (mg/L)	11	105.07	119.42	85.03	24.33	249.11
TN (mg/L)	11	111.75	89.23	51.15	9.92	177.63
TP (mg/L)	9	14.38	16.77	12.56	3.05	42.25
SO_4 (mg/L)	11	97.20	91.27	29.01	43.44	128.53
Fats oils grease (mg/L)	9	6.32	20.43	24.82	2.41	60.32
Detergents (mg/L)	6	0.18	0.18	0.07	0.08	0.26
PO_4 (mg/L)	11	7.25	8.27	6.21	1.42	21.72
NH_3 (mg/L)	5	6.89	25.08	34.88	0.10	82.97
NO_2^- (mg/L)	2	1.75	1.75	0.90	1.12	2.39
Organohalogens (mg/L)	3	0.01	0.01	0.00	0.01	0.01
Toluene (mg/L)	3	0.00	0.02	0.03	0.00	0.06
Organic solvents (mg/L)	3	0.01	0.01	0.00	0.01	0.01
Cyanides (mg/L)	3	0.01	0.01	0.00	0.01	0.01
DMSO (mg/L)	3	3.90	7.30	9.37	0.10	17.90
Copper (mg/L)	2	0.01	0.01	0.00	0.01	0.01
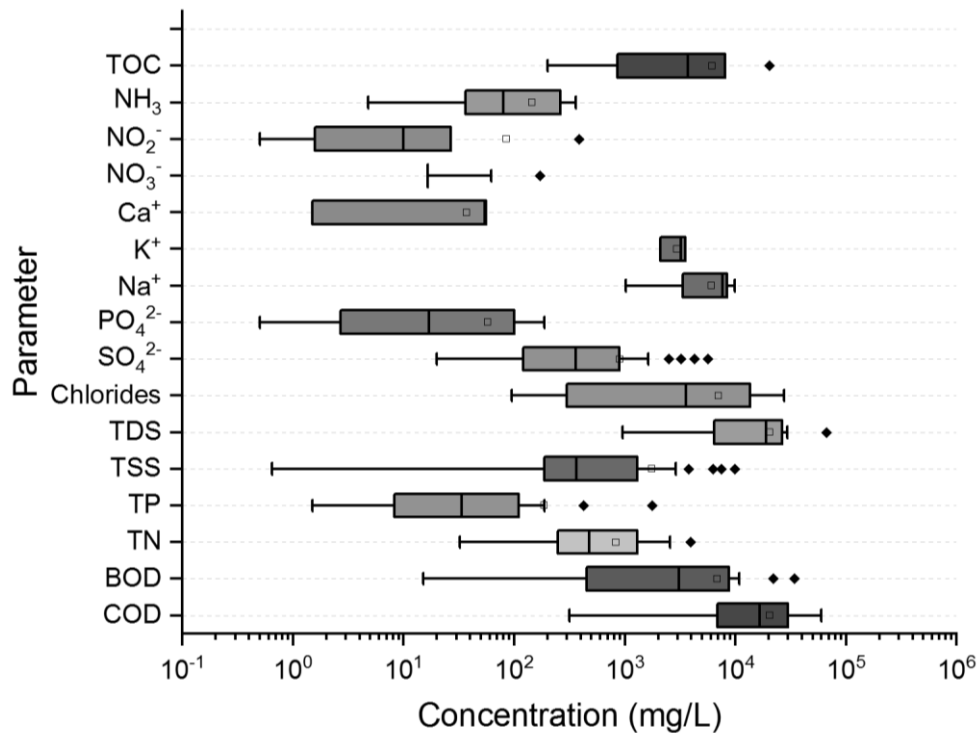
Figure 15 Concentrations of selected compounds and aggregate measurements for the biopharmachem industry

The selection of parameters monitored in Irish biopharmachem TE licences is typically specific to the processes being undertaken at a given site, however there are some commonalities between licences as shown by the frequency for monitored parameters summarised in Table 5. Organic solvents are commonly used during the synthesis, and purification of drug compounds, and these solvents often come into contact with water that is later disposed of as TE. The recovery of these solvents is performed where economically feasible since these solvents are often expensive, however disposal of solvents in TE to sewer or as fuel for energy production are alternative strategies (Bielen et al., 2017). Specific compounds of concern that may be discharged from the chemical and biopharmaceutical industries include benzene, toluene, chlorinated solvents such as dichloromethane and chloroform are monitored in appropriate licences and these compounds contribute to organic loadings (Dsikowitzky and Schwarzbauer, 2014; Sharif et al., 2016).

Due to the high COD and BOD levels in biopharmaceutical effluent, anaerobic bioreactors are often utilized to reduce these parameters prior to discharge to sewer, due to their effectiveness and low operation costs (Shi et al., 2017). These anaerobic processes generate quantities of short and medium chain fatty acids (Cetecioglu et al., 2015) as a result of the degradation of materials in anoxic conditions. Treatment of pharmaceutical wastewater using digestion processes can be

complicated by the presence of high levels of antibiotics along with organic reagents that are commonly toxic to biological organisms that are performing these processes (Xing et al., 2014).

Waste management

Waste management usually involves (i) material transfer of wastes for recycling or recovery, (ii) composting and anaerobic digestion, (iii) recovery of energy from waste and (iv) disposal of residual wastes to landfill. The management of waste by these activities generates a range of different TE streams that have unique challenges. The characteristics of wastewater effluent from waste management sites is highly dependent on the nature of the processing taking place at a given site at the time of sampling. Typical waste disposal techniques in Ireland are focused on recycling and energy from waste strategies, while landfills have historically been used for waste disposal. Legacy landfills yield wastewater in the form of leachate. It has been reported that leachate can solubilise components of landfill contents and transport dissolved material to the environment (Deng and Englehardt, 2006; Gao et al., 2015). Modern engineered landfills are designed to prevent movement of leachate into the aquatic environment. Water used during recycling similarly can solubilise compounds from solid and liquid waste to TE containing inorganic nutrients, organics and metal species that require monitoring.

Table 6 Summary of licensed parameters for the Irish AER data related to the waste management sector

Parameter	n	Median	Mean	SD	Min	Max
pH	18	7.55	7.64	0.62	6.42	9.26
Temperature	11	11.8	19.7	14.5	9.5	44.0
Volumetric flow (m^3/day)	3	48.14	45.77	4.94	40.09	49.08
Annual water emission (kg)	3	6.E+06	6.E+06	2.E+06	4.E+06	8.E+06
COD (mg/L)	18	463.13	965.27	1503.20	98.27	5140.00
BOD (mg/L)	15	112.75	190.75	201.33	45.75	860.09
TSS (mg/L)	18	131.13	249.33	294.39	16.55	1151.50
TP (mg/L)	9	3.89	46.07	59.02	1.57	132.00
SO_4 (mg/L)	15	92.93	202.70	230.97	31.79	823.00
Fats oils grease (mg/L)	15	2.89	7.60	8.41	0.20	25.00
Detergents (mg/L)	15	0.68	4.50	13.50	0.20	53.23
PO_4 (mg/L)	6	3.06	19.40	40.40	1.08	101.78
NH_3 (mg/L)	9	82.50	125.45	113.58	4.13	279.63
NO_3^- (mg/L)	3	5.67	5.91	0.70	5.36	6.70
Copper (mg/L)	6	0.02	0.03	0.02	0.01	0.05
Chlorides (mg/L)	6	166.65	1230.64	1782.04	22.88	4030.00
Zinc (mg/L)	6	0.11	0.22	0.21	0.05	0.52
Mineral oils (mg/L)	9	2.31	103.83	305.39	0.20	918.20
Phenols (mg/L)	3	0.02	0.33	0.56	0.01	0.98
Lead (mg/L)	6	0.01	0.01	0.01	0.01	0.02
Cadmium (mg/L)	3	0.00	0.00	0.01	0.00	0.01
Chromium (mg/L)	3	0.10	0.09	0.03	0.06	0.11
Nickel (mg/L)	3	0.04	0.04	0.00	0.04	0.04
Arsenic (mg/L)	3	0.04	0.04	0.01	0.03	0.04
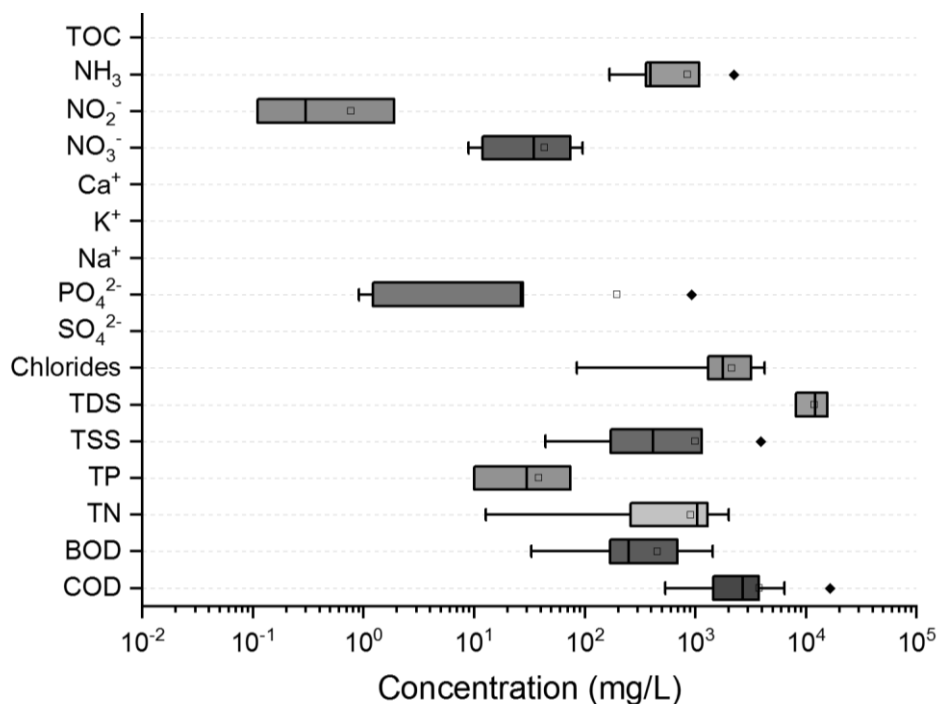
Figure 16 Concentrations of selected compounds and aggregate measurements for the waste management industry

Examples of parameters that are monitored in Irish TE licences are shown in Table 6, and compared in Figure 16. Similar to the biopharmachem waste stream heavy metals are monitored in these licences due to the disposal of waste and potential for leachates from recycling or landfill sites. Other types of compounds that are potentially present in waste management effluent include tannins, phenolics (Lacorte et al., 1999), alkaloids, carbohydrates, resin compounds, long chain fatty acids, resin acids, volatile terpenes and phosphorous/nitrous compounds (Bueno et al., 2012; Cardenas et al., 2016) all of which can contribute to the nutrient and organic load in TE.

Conclusions and future opportunities

The variability in TE composition is substantial, both between different TE sectors and between companies within a general sector, due to the wide variety of processes carried out. For example, in the food and beverage industry the nature of dairy wastewater compared to that of a distillery is understandably very different. To overcome the complexity of TE analysis, industry and environmental regulators have developed and implemented chemical and physical tests that provide useful information on the composition of TE that is relevant to sewer integrity and downstream WWTP operation. Measurements of effluent flow rate, temperature and the size and amounts of particulate and solids are important physical properties as these are valuable for the prevention of sewer blockages or overflows; while chemical tests quantify bulk nutrients,

inorganic/organic compounds and metals that are the target of WWTP treatment prior to the release of water back to the natural environment. The composition of TE can vary significantly over relatively short periods of time leading to spike concentrations of components being emitted to sewers (Hauser et al., 2019). Sample collection and analytical throughput are the largest barriers to obtaining time resolved information about the composition of TE. While high frequency sampling provides more information about how TE composition varies over time, this approach is time and resource expensive. Composite sampling has been used as a means to increase the representativeness of TE samples, however it requires the collection of large volumes of sample that can be challenging to analyse. Monitoring TE parameters is essential for maintaining compliance with environmental regulations; however, the practical limitations of time and resources are providing a driving force for investigating new sampling and analysis technologies for monitoring. The present focus on analysing TE with physicochemical and wet chemical analytical techniques perhaps not ideal in terms of informing the composition of TE in a rapid and robust way.

Passive sampling can potentially enhance capabilities for the analysis of TE by providing composite sampling without the need to collect and process large volumes of TE (Sonavane et al., 2018). Passive sampling selectively absorbs and concentrates compounds of interest from TE over the course of a devices deployment which allows the calculation of time weighted concentration averages or mass loadings when combined with volumetric flow data (Castle et al., 2018; Charriau et al., 2016). The main limitations of passive samplers include their focus on dissolved compounds, since particulates are not absorbed by these materials, additionally the determination of compound uptake rates requires some optimisation prior to use of the technique (Lissalde et al., 2016). Passive sampling is also not prescribed for regulatory purposes at this time due to the ongoing development of the technology and current requirements for TE monitoring. Novel sensor technologies go one step further and alleviate both the need to take large or frequent water samples, as well as facilitate real time data collection on licensed parameters and surrogates of licensed parameters (Boënne et al., 2014; Qin et al., 2012, 2018). There are a wide variety of sensor technologies that are commercially viable such as those summarised in Table 3. These sensors can generate data useful for observing regulatory compliance, but also deliver predictive capabilities that will allow industry to control the properties of their TE (Qin et al., 2012). Spectroscopic and chemical sensors are showing great promise in TE monitoring. For example, COD measurements are one of the essential parameters monitored in TE, however this test generates large quantities of heavy metal waste resulting from the use of chromate as the oxidant that is costly to dispose of; research into UV-Vis (Brito et al., 2014; Chen et al., 2014), fluorescence (Lee and Ahn, 2004; Reynolds, 2002) and near-infrared (NIR) (Dahlbacka et al.,

2014; Sarraguça et al., 2009; Sousa et al., 2007) spectroscopy have shown promise in determining COD levels without the need for wet chemistry techniques. The challenges of dealing with particulates and sample dilution required when working with spectroscopic techniques limit the application of these techniques however ongoing research using approaches such as variable path length UV-Vis combined with regression techniques can overcome this limitation (Chen et al., 2014). Another approach utilises laser-induced break down in combination with UV-Vis spectrophotometry for purposes of estimating COD without the need of chemical digestion prior to measurement (Ye et al., 2018). Similarly these spectroscopic approaches have been extended to allow measurements of licensed parameters like TSS (Brito et al., 2014; Sarraguça et al., 2009), and BOD (Jouanneau et al., 2014; Reshetilov et al., 2013), highlighting the exciting potential of sensors for use as surrogate measures of licensed TE parameters. Solid state sensors are capable of detecting a wide variety of heavy metallic, inorganic and organic compounds (Zhuiykov, 2012). However, the selectivity of these sensors is not ideal due to the similarities between many target compounds. To overcome this limitation researchers have developed sensor arrays that utilize advanced data analysis techniques to enhance the metal identification capabilities of sensor arrays (Zulkifli et al., 2018; Arduini et al., 2017; Gholizadeh et al., 2016).

The implementation of passive sampling and sensor technologies is promising for improving industries knowledge about the composition of TE relevant to licensed parameters. Both approaches provide the ability to directly measure or obtain surrogate information linked to licensed parameters, and the TE that will allow industries to better manage their TE.

2 Characterisation of trade effluent

Characterisation of TE

Introduction

This project is focused on three main goals of; (i) characterising TE from three high risk sectors, (ii) identifying markers or surrogate parameters in TE, and (iii) investigating the applicability of novel sensor technology for monitoring. This research will enable industry and Irish Water to adopt a preventative approach to TE monitoring, optimise resource usage, and reduce monitoring burdens of TE.

This section is focused on goal (i) characterising TE from three high risk sectors. This involved analysing TE using a wide range of organoleptic and chemical analysis techniques to provide information on the levels of organics inorganics, nutrients and metals in TEs from the biopharmachem, food/beverage and waste management sectors. Information on the levels of these species in TE is useful for providing insight into effluent composition and variation, which informs the deployment of real-time monitoring and passive sampling strategies. These monitoring tools are potentially valuable as they can provide capabilities to control loadings of these species released to sewer.

In addition to the organoleptic and wet chemistry analysis techniques that are currently used for monitoring TE, a range of additional analytical techniques were applied to expand knowledge in TE composition. Gas, liquid and ion chromatography along with MS and spectroscopy were employed to provide detailed information on specific chemical compounds. This data on the composition of TE samples will be used to inform levels of input to sewer systems and the selection sensor and passive sampler technologies for monitoring TE properties. Furthermore, this data set will enable the identification of appropriate markers, or surrogate species, for monitoring licensed parameters within TE.

Methods

Sample collection and preservation

Hydrochloric acid 37 % w/v (#30721) and sodium hydroxide pellets (#30620) were purchased from Sigma Aldrich (Ireland). Three samples of TE were collected during each sampling instance to satisfy the requirements of analysis. Duran 500 mL plastic coated borosilicate bottles (#Z153893, Sigma Aldrich) and Nalgene HDPE bottles with polypropylene screw caps (#15656718, Fisher Scientific, Ireland) were used as sample containers. Table 7 details the storage conditions of the samples that were collected. At the time of sampling each container was rinsed with TE three times before being filled to the top to exclude oxygen and sealed. TE samples

were transported from industrial sites to the laboratory in ice filled coolers. Two of the samples were acidified to pH 2 for preservation using hydrochloric acid (6 mol/L) and all samples were refrigerated at 4 ℃ until analysis was performed.

Table 7 Sample collection containers, additions and storage conditions

Storage condition	Sample container	Volume (L)	Additions
1	Borosilicate	0.5	Acidified with hydrochloric acid to pH 2
2	High density polyethylene	1	No additions
3	High density polyethylene	1	Acidified with hydrochloric acid to pH 2

Note that some assays require preserved, unpreserved or specific sampling container materials (polyethylene or borosilicate) to generate valid results. Please refer to the standard methods of water and wastewater analysis handbook for further information on these requirements (American Public Health Association et al., 2017).

Wet chemistry and organoleptic analysis

Wet chemistry reagent kits were purchased from HACH-Lange (Cork, Ireland) for the measurement of COD, TOC, TN, TP, phosphate, nitrite, nitrate and ammonia. The parts and descriptions of each of these kits are summarised in Table 8 along with their respective HACH method references.

Table 8 Wet chemistry reagent kits used and HACH reference methods

Part Number	Analyte	Description	HACH Method
2345952	COD	COD TNT, 0-15000 mg/L O_2	8000
2606945	NH_3	Nitrogen, Ammonia TNT, 0.4-50 mg/L NH_3-N	10031
2608345	NO_2^-	Nitrite Nitrogen Reagent Set, 0.003 to 0.500 mg/L as NO_2-N 50 tests	10019
2605345	NO_3^-	Nitrate TNT, 0.2-30 mg/L NO_3-N	10020
2767345	PO_4	Orthophosphate, TNT, 1.0-100 mg/L PO_4	8114
2714100	TN	Nitrogen, total, TNT, 10-150 mg/L N	10072
2815945	TOC	TOC (Purging Method) TNT, 15-150mg/L C	10128
2767245	TP	Phosphorous, total, TNT, 1.0-100 mg/L PO_4	10127

A DR900 colorimeter (Hach-Lange, Ireland) was used for spectroscopic measurements and quantification of the targeted wet chemistry parameters. In cases where the concentration of a

nutrient exceeded the calibration range of the reagent kit an appropriate dilution was performed to allow accurate quantitation.

Sensor and spectroscopic analysis

Measurements of pH and conductivity were carried out using a WTW Multi 3320 metre (VWR, Ireland) equipped with a SenTix pH and conductivity probe (#C171713043, Xylem, Ireland). A 30 mL volume of each sample was transferred to a 50 mL polypropylene tube and allowed to equilibrate at room temperature prior to pH and conductivity measurements. Turbidity was measured with a WTW TURB 430 IR turbidimeter (Xylem, Ireland). Samples were allowed to equilibrate to room temperature and transferred to 25 mL scintillation vials prior to turbidity measurements. All pH, conductivity and turbidity measurements were performed in triplicate.

UV-Vis measurements were carried out using a Shimadzu UV-1800 model UV-vis spectrophotometer (Mason Technologies, Dublin, Ireland). Wastewater samples were filtered with a 10 mL polypropylene syringe and a 0.45 µm pore size syringe filter (Whatman GD/XP, PFDV membrane, Merck, Ireland) to remove particulates. Samples were transferred to a 1 cm pathlength quartz cuvette. UV-vis spectra were collected at 1 nm resolution across the range of 190 to 800 nm in triplicate and averaged using UVProbe software (Version 2.33, Shimadzu, Ireland).

Ion chromatography analysis

Sodium carbonate (#791768), sodium hydrogen carbonate (#1063290500), sodium fluoride (#201154), sodium chloride (#43320-9), sodium nitrate (#1065370500), sodium phosphate (#S9638) and sodium sulphate (#239313) were purchased from Sigma Aldrich, Ireland. Sodium nitrite (#424350020) was purchased from ACROS organics (Ireland). Calibration solutions were prepared to cover the 0.1 to 100 mg/L range.

IC was performed using a Dionex ICS-3000 instrument (ThermoFisher Scientific, Ireland) equipped with a Dionex AS autosampler (ThermoFisher Scientific). Separations were carried out using a Dionex IonPac AS-12A column (2 × 200 mm, P/N 046055, ThermoFisher Scientific) with a 10 µL sample injection loop. Separation was carried out isocratically using an eluent composed of 2.7 mM sodium carbonate with 0.3 mM sodium hydrogen carbonate dissolved in deionized ultrapure water (resistivity 18.2 MΩ/cm), with a flow rate of 0.38 mL/min and a separation time of 15 min. A Dionex ARS-ULTRA II 2 mm anion self-regenerating suppressor (#061562, ThermoFisher Scientific) with an operating current of 6 mA was used for supressing background eluent conductivity. Peak detection was performed using a Dionex conductivity cell with a 10 mm path length (#061830, ThermoFisher Scientific) that was operated at a data collection rate of 5

Hz with a rise time of 0.5 s. The column and detector compartments were maintained at 30 °C, while the detector cell was maintained at 35 °C. Data were collected and processed using Chromeleon 7 Chromatography Data system (version 7.2 SR4 8179, ThermoScientific, Ireland).

Organics analysis

Pesticide grade dichloromethane was purchased from Fisher Scientific (Dublin, Ireland). LC-MS grade acetonitrile and Whatman GF/F filter glass fibre filters, a 24 component saturated *n*-alkane mixture ranging from *n*-heptane to *n*-triacontane dissolved in *n*-hexane (PN# 49451). Were purchased from Sigma Aldrich (Arklow, Ireland). Deionised water with a resistivity of 18.2 MΩ/cm was obtained from an ELGA Pure Lab Ultra deionized water purifier (VWR, Dublin, Ireland). Oasis Hydrophilic Lipid Balance (HLB) SPE cartridges with a 6 mL tube size, 60 μm particle size and 150 mg bed mass were used for the extraction of organics (Waters Chromatography, Dublin, Ireland). EPA 8270 semivolatiles CLP method Base Neutral Surrogate mixture (PN# RE31062) containing nitrobenzene-d_5, 2-fluoro-biphenyl and *p*-terphenyl-d_{14} in dichloromethane, EPA 8270 semivolatiles internal standard mixture in dichloromethane (PN# RE31006) containing Acenaphthene-d_{10}, Chrysene-d_{12}, 1,4-Dichlorobenzene-d_4, Naphthalene-d_8, perylene-d_{12}, phenanthrene-d_{10} and EPA 8270 semivolatiles mixture containing 76 components in dichloromethane (PN# RE 31850) was purchased from Restek Thames (Saunderton, United Kingdom).

Triplicate samples (100 mL each) of each TE sample were spiked with a concentration of 1 mg/L of surrogate standards prior to extraction. After addition of the internal standard mixture, each sample was inverted 30 times and transferred to a refrigerator to equilibrate overnight before being vacuum filtered through a Whatman GF/F glass fibre filter to remove particulates larger than 0.7 μm in diameter. Oasis HLB SPE cartridges were conditioned on a 20-port vacuum manifold (Waters, Ireland) with 6 mL of dichloromethane, followed by 6 mL acetonitrile and finally 6 mL of deionized water prior to loading TE samples. Each sample was loaded onto a labelled SPE cartridge using vacuum assistance and a controlled flow rate of approximately 5 mL/min. The SPE cartridges were then dried by drawing air through the cartridges for 30 min, after which 6 mL of dichloromethane was used to elute the organics loaded from each SPE cartridge into a labelled 14 mL borosilicate test tube vial (Fisher Scientific, Ireland). The volume of dichloromethane was reduced to 0.5 mL under a stream of dry nitrogen gas and a mixture of internal standards were then added to achieve a concentration of 1 mg/L.

An Agilent 6890 gas chromatograph (Agilent Technologies, Cork, Ireland) equipped with a split/splitless injector, an Agilent 7683 series automated liquid sampler and an Agilent 5973

Network Mass Selective Detector was used for analysis of the SPE extracts of each TE sample. A weakly polar VF-5ms column (Agilent, Ireland) coated with 5% phenyl-/95% dimethyl-polysiloxane polymer equivalent. The column was 30 m long with an internal diameter of 250 μm and a stationary phase film thickness of 0.25 μm. This column was selected based on recommendation provided by EPA Method 8270 for the analysis of semi-volatile organics (US EPA, 2019).

The inlet temperature was set to 250 ℃ and operated in the pulsed splitless mode with a head pressure of 30 PSI held for 0.6 min during sample injection. A volume of 1 μL was injected for all samples. The carrier gas was helium (Air Products, Dublin, Ireland), which was set to provide a column flow rate of 1.2 mL/min. The injector was operated in splitless mod for 2 min after which the liner was purged with a flow rate of 100 mL/min for 1 min. The GC oven was programmed from an initial temperature of 40 ℃ which was held for 1 min, and then ramped at 25 ℃/min to 280 ℃, followed by ramping at a slower rate of 5 ℃/min to a final temperature of 320 ℃ which was held for 1 min. The total separation time was 19.6 min. The MS transfer line was set to a temperature of 280 ℃. The mass spectrometer was operated with a source temperature of 180 ℃, a quadrupole temperature of 150 ℃ and a detector voltage of 70 eV. Data was acquired from 2.2 to 19.6 min from 35 to 550 m/z at a scan rate of 5.36 scans /s. Compound identities were determined using library searching with NIST 98 Mass Spectral Library (Agilent) and further confirmed using retention index matching and comparison with authentic compound standards. Quantitation was performed using Agilent Chem Station based on calibration with a series of solutions with concentration ranging from 5000 to 1 μg/L.

Metals analysis

Concentrated nitric acid (70 % w/w, PN# 438073) and hydrochloric acid (37 % w/w, PN# 30721) specified for trace metals was obtained from Sigma Aldrich (Ireland). Borosilicate glassware, including 100 mL volumetric flasks, 250 mL beakers and watch glasses were purchased from Fisher Scientific (Ireland). All glassware was acid soaked for 24 h in 6 mol/L hydrochloric acid and rinsed with deionized water (18.2 MΩ/cm) and allowed to dry in an oven (120 °C, overnight) prior to use. An ICP standard (Periodic table mix 1 for ICP in nitric acid) containing 33 elements (10 mg/L each) was purchased from Sigma Aldrich (Ireland) at including Al, As, Ba, Be, Bi, B, Ca, Cd, Cs, Cr, Co, Cu, Ga, In, Fe, Pb, Li, Mg, Mn, Ni, P, K, Rb, Se, Si, Ag, Na, Sr, S, Te, Tl, V and Zn in 10 % nitric acid (10 mg/L each).

TE samples were digested using the nitric acid digestion protocol specified in APHA Method 3030E (American Public Health Association et al., 2017). A volume of 100 mL of each sample

was added to an acid cleaned 250 mL borosilicate beaker and capped with a watch glass. Samples were the placed on a hot plate set to boil, and 5 mL of concentrated nitric acid (70 %) were added to each sample container. Samples were boiled and reduced in volume to 20-30 mL, and the walls and capping watch glass were periodically rinsed down into the beaker using deionized water to ensure complete digestion of particulates. Samples were digested until a clear or light yellow colour solution was achieved. Samples were then removed from the hotplate and allowed to cool to room temperature before being transferred to 100 mL volumetric flasks. The containing beaker was rinsed with two volumes of 5 mL deionized water, which was then transferred to the volumetric flask. Each flask was then made up to the mark in preparation for analysis by ICP-OES.

A Varian-MPX CCD Simultaneous ICP-OES (Elementec, Ireland) was used for the measurement of spectral wavelengths corresponding to a range of metals in each sample. Varian ICP-Expert, ICP-OES instrument software (Version 4.1.0) was used for instrument control and data acquisition. The wavelengths were monitored for each metal are summarised in Table 9. Note that some metals were monitored at multiple spectral wavelengths to check for spectral interferences from metals with similar emission wavelengths.

Table 9 ICP-OES spectral wavelengths monitored for target metals. Al, Bi, Cu, Mg, Mn and Zn were monitored at two wavelengths for quality control purposes

Element	Wavelength (nm)	Element	Wavelength (nm)	Element	Wavelength (nm)
Ag	328.068	Fe	259.940	S	181.972
Al	237.312	Ga	417.204	Se	196.026
Al	396.152	In	230.606	Si	251.611
As	188.980	K	766.491	Sr	407.771
Ba	455.403	Li	670.783	Te	214.282
Be	313.042	Mg	279.553	Tl	190.794
Bi	223.061	Mg	285.213	V	292.401
Bi	249.772	Mn	257.610	Zn	206.200
Ca	396.847	Mn	279.482	Zn	213.857
Cd	214.439	Na	589.592		
Co	238.892	Ni	231.604		
Cr	267.716	P	213.618		
Cu	224.700	Pb	220.353		
Cu	324.754	Rb	780.026		

Calibration was performed using a mixture of the metals listed Table 9 across a range of concentrations of 10 to 0.05 mg/L. Digested samples were diluted as necessary to allow quantification in this calibration range.

Results and discussion

A wide range of organoleptic and chemical analysis techniques were utilised to determine the levels and variation in properties of TE for the biopharmachem, food/beverage and waste management sectors. Before considering the results of the analysis it is important to consider the impact that sample collection can have on TE analysis. Industrial enterprises can produce significant volumes of TE that vary in properties over short and long timespans. It is important that the samples collected are representative of a site's TE over time, while not requiring excessive costs in terms of time and capital expenditure to complete the characterisation of samples.

During this project samples were collected in either the composite or grab sampling mode, with a preference for composite sample collection as they are more representative of the average composition of a TE stream. The composite samplers in use were operated over 24 h durations, sampling at intervals of 15 to 30 min. The main cause of composite samples being unavailable for this study was that the composite samples were being utilised for regulatory monitoring and insufficient sample volume was available for the additional analysis required by this project. If no

composite sample was available at a site, then grab sampling was performed instead. Grab sampling was preferentially performed on balancing tanks after any treatment processes, since the large volume of these tanks provided a time weighted average of effluent composition linked to the tanks holding time (typically 3 to 12 h duration). Finally, if grab sampling from a holding tank was not feasible, then a grab sample was taken from the sites TE outlet to sewer providing a snapshot of the composition of effluent for that site. Table 10 summarises the properties of the samples evaluated in the present report. Samples were taken from composite samplers for 6 sites and 2 grab samples were taken from balancing tanks to yield pseudo-composite samples. Finally, 2 samples were obtained in the grab format from outlet pipes from balancing tanks releasing to sewer.

Table 10 Details of samples taken from sites including on-site processes, treatment, balancing additions and the type of sample taken

Site	TE sector	Process	On-site treatment	pH balancing additions	Sample type	Sampling location
1	Bio pharma-chem	Biomolecule drugs	pH balancing, temperature reduction	Sodium hydroxide, sulphuric acid	Composite	Sampler
3		Small molecule drugs	pH balancing	Sodium hydroxide, sulphuric acid	Grab	Balancing tank
4		Biomolecule drugs	pH balancing	Sodium hydroxide, hydrochloric acid	Sample type	Sampler
5		Small molecule drugs	pH balancing, denitrification	Sodium hydroxide, hydrochloric acid	Grab	Balancing tank
6	Food/ beverage	Food products	pH balancing, denitrification, dissolved air flotation	Sodium hydroxide, hydrochloric acid	Composite	Sampler
7		Beverages	pH balancing, temperature reduction	Sodium hydroxide, sulphuric acid	Composite	Sampler
8		Beverages	pH balancing, dissolved air flotation, temperature reduction	Sodium hydroxide, hydrochloric acid	Composite	Sampler
9		Food products	pH balancing, dissolved air flotation	Sodium hydroxide, hydrochloric acid	Grab	Outlet pipe
10		Food products	pH balancing, dissolved air flotation	Sodium hydroxide, hydrochloric acid	Composite	Sampler
11	Waste Mgt.	Recycling	pH balancing	Sodium hydroxide, hydrochloric acid	Grab	Outlet pipe
12		Recycling				
13		Landfill	pH balancing, filtration	Sodium hydroxide, hydrochloric acid	Composite	Sampler
14		Landfill	No treatment	NA	Composite	Holding tank
15		Landfill	No treatment	NA	Composite	Holding tank

The biopharmachem sites could be divided into two categories that produced either biopharmaceuticals or small molecule drugs. Food/beverage companies were divided into food

processing (meat and dairy) and beverage production (alcoholic and non-alcoholic) categories. Waste management sites could be divided into landfill management and recycling streams. All sites (other than two landfill leachate generating sites) performed pH balancing of their TE prior to release and samples were collected at or after the point of pH balancing to ensure that samples were all collected at conditions matching the release conditions. All sites used sodium hydroxide to increase pH, while either hydrochloric (7 of 10 sites) or sulphuric acid (3 of 10 sites) were used for reducing effluent pH. The selection of sulphuric acid or hydrochloric acid as pH a balancing additive will cause increased levels of the sulphate or chloride anions in the outputted TE respectively, which should be considered when interpreting the outputs from a site. Two of the landfill leachate producing waste management sites did not perform any treatment on their TE, however these sites were not releasing their leachates to sewer and were instead sending it to WWTPs using specialised waste disposal companies using shipment containers or tankers.

In addition to pH balancing, three sites incorporated heat exchange setups for reducing the temperature of TE prior to release and all sites had temperature sensors installed to monitor the temperature of released effluent. Some additional advanced treatment options were also used for the purposes of reducing various TE parameters prior to release to sewer. In the food/beverage industry the application of dissolved air flotation was used in 50 % of sites for the removal of COD and particulates generated during production. Denitrification using bacterially mediated aerobic degradation was performed at three sites (biopharmachem and food/beverage sites) to reduce loads of ammonia, nitrite and nitrate species. One waste management site used membrane purification to reduce the presence of organic and inorganic compounds in TE prior to release to sewer. An evaluation on the efficiency of these various post process treatment options was not performed, as this project is focused on the overall characteristics of TE being released to sewer networks. However, TE treatments strategies, such as dissolved air flotation and denitrification processes, can substantially impact the composition of TE which is important to consider when comparing the variation in properties of different sites. Furthermore, knowledge on the impacts of different treatment strategies is valuable for generalizing the findings of this report to other industrial sites.

Visual properties

Samples were characterized qualitatively by visual inspection and the results of this analysis are shown in Table 11, including details of TE colour, turbidity/suspended solids and indications about the properties of any sediments present in the samples.

Table 11 Summary of visual characteristics of TE samples

Site	Sector	Colour	Turbidity/Suspended solids	Sediment
1	Biopharma-chem	No colour	None	Small portion of light brown small particulates
3		Light orange	Opaque, no large suspended solids	Small granular particulates, white, forming a layer
4		Light yellow	None	Small granular particulates, brown/orange like sand
5		Yellow, off-white	Opaque, no large suspended solids	None
6	Food /beverage	Light orange/yellow	Minimal turbidity, no large suspended solids	Layer of light brown granular particulates
7		Light orange/brown	Opaque, no large suspended solids	Orange/brown sediment, fine particles
8		No colour	Opaque white suspended solids, small particulates	Small amount of white particulates
9		Green/brown	Minimal turbidity	Moderate amount of fine, dark brown particulates
10		Clear	Minimal turbidity	Opaque, white/off-white particulates
11	Waste mgt.	No colour	Minimal turbidity caused by dirt like particulates	Small dirt like particulates, brown/grey
12		Clear	Moderate turbidity, dirt like particles	Small amounts of brown particulate sediment
13		No colour	None	Almost none, a few fine dirt particulates
14		Green/brown	Moderate turbidity, small particles	Few fine particulates
15		Green/brown	Minimal turbidity	Few fine particulates

Samples varied substantially in their physical characteristics both within and across sectors. For example, samples derived from biopharmachem and food/beverage sites displayed a wide variety of colours from clear to light yellow, yellow, orange and green. All of the samples obtained from the food/beverage sector had moderate to high levels of turbidity, and the samples from this sector had the largest amounts of sediment compared the other two sectors. Biopharmachem samples generally had low amounts of TE sediments, although there were still appreciable quantities in half of the samples. Three of the waste management samples (11, 12, 13) had minimal or no turbidity with little evidence of colour or sediment. While, the two remaining waste management sites (14 and 15) had stronger colours and particulate loadings. These two sites were producing

landfill leachates which were removed by tanker, rather than being released to sewer networks directly.

Odour characteristics

The odour of each sample was qualitatively assessed using descriptors and a strength rating as tabulated in Table 12. The biopharmachem samples had relatively low amounts of odour with somewhat artificial or stagnant odours that could arise from solvent usage. Food/beverage samples derived from dairy or beverage companies yielded low levels of odour with sweet/artificial or just a minimal stagnant smell suggesting of the presence of some organics. TE from site 6 had a foul/artificial odour that suggested degradation of organic matter. Three of the waste management (11 and 13) samples collected indicated low odours. Sites 14 and 15 had strong in odours due to them being untreated landfill leachates rather than treated TE like the other waste management samples.

Table 12 Odour and odour strength characteristics of samples from TE sectors. Odour strength measured on a 4-point scale 0 = no apparent odour, 1 = mild, 2 = moderate, 3 = strong

Site	TE sector	Odour description	Odour strength
1	Biopharmachem	Stagnant water	1
3		Artificial, sweet	2
4		Stagnant water	1
5		None	0
6	Food/beverage	Stagnant water	1
7		Foul, artificial	3
8		Sweet, artificial	1
9		Stagnant water	1
10		Organic, artificial	2
11	Waste management	Stagnant water	1
12		Off, stagnant	2
13		Odour less	0
14		Off, stagnant	3
15		Off, stagnant	3

Wet chemistry analysis

Samples from each site were analysed using a panel of wet chemistry techniques, in addition to pH, conductivity and turbidity measurements with ion selective electrodes/sensors. The pH parameter is important to monitor due to its impact on sewer chemistry and potential effects on other parameters, such as conductivity. However, the widespread use of pH balancing in industry

limits the utility of this parameter as a surrogate measure of any other monitored parameters. Conductivity measurements provide a measurement of a samples ability to carry an electrical current, which is a composite parameter dependent on solution composition including metals, organic and inorganic species, ionic strength, pH and temperature. Due to the universal response of conductivity sensors to many TE parameters, this sensor could be useful for detecting changes in levels of organics, inorganics and metallic components in a TE stream. For example a biopharmachem company may buffers and salts during production of a protein-based drug which would impact the conductivity its outputted TE. Similarly turbidity sensors can be used to inform levels of suspended solids, COD and other nutrient parameters as the particulates that cause turbidity can contribute strongly to these parameters. Wet chemistry measures were carried out with reagent kits designed to provide information on monitored parameters. The results of the analysis of the biopharmachem (Table 13), food/beverage (Table 14) and waste management (Table 15) sectors are summarised below.

Table 13 Biopharmachem sector wet chemistry results summary

Measurement	Median	Mean	SD	Max	Min
Ammonia	8.0	56.9	87.6	185.0	<LOD
COD	1005.0	5576.2	11042.9	30100.0	110.0
Conductivity	4.0	6.5	8.5	23.4	0.7
Nitrate	0.4	0.5	0.5	1.2	<LOD
Nitrite	0.0	0.4	0.7	1.4	<LOD
pH	7.2	7.2	0.8	8.4	6.1
Phosphate	30.0	118.2	189.7	402.0	11.0
TN	19.0	60.4	94.8	250.0	4.7
TOC	214.0	1449.3	2632.5	6711.7	53.7
TP	10.9	28.7	37.4	100.0	3.5
Turbidity	32.9	206.6	419.3	1061.1	14.8

The biopharmachem samples showed low variation in the pH parameter (7.2 ± 0.8). Conductivity varied over 2 orders of magnitude while turbidity varied over 3 orders of magnitude. There was also substantial variation in the TOC, COD (3 order of magnitude), while TN, ammonia and phosphate parameters varied over narrower ranges.

Table 14 Food and beverage sector wet chemistry results summary

Measurement	Median	Mean	SD	Max	Min
Ammonia	2.0	2.9	3.2	8.0	<LOD
COD	273.3	2068.9	2877.1	7623.3	51.3
Conductivity	2.7	4.3	3.4	11.1	1.9
Nitrate	0.6	0.6	0.2	0.9	0.3
Nitrite	0.0	0.1	0.2	0.4	<LOD
pH	6.8	6.4	0.8	7.4	5.3
Phosphate	25.4	26.7	18.4	49.6	6.6
TN	14.7	22.2	23.0	66.3	2.0
TOC	136.3	555.6	680.4	1940.0	48.7
TP	3.3	18.4	30.2	73.6	<LOD
Turbidity	26.6	129.7	239.8	711.3	1.8

The pH of the food/beverage sector was slightly more acidic compared to the biopharmachem industry, although it showed similar variance (6.8 ± 0.8). The conductivity of these samples showed low variance varying over just 1 order of magnitude, while turbidity varied over 2 orders of magnitude. Significant variance was found in the COD, TOC, TN, TP parameters.

Table 15 Waste management sector wet chemistry results summary

Measurement	Median	Mean	SD	Max	Min
Ammonia	50.0	60.6	76.0	190.0	2.0
COD	120.0	455.5	767.5	1826.7	66.7
Conductivity	1.5	2.8	3.8	9.3	0.1
Nitrate	0.6	0.6	0.4	0.9	0.3
Nitrite	0.1	0.1	0.1	0.1	<LOD
pH	7.2	5.9	2.3	7.4	1.9
Phosphate	7.5	7.5	9.8	14.4	0.6
TN	73.3	86.9	85.3	226.7	14.7
TOC	51.0	159.9	204.1	513.7	26.7
TP	0.0	1.0	1.4	2.8	<LOD
Turbidity	23.0	36.9	48.7	122.4	0.0

The pH of waste management samples was centred around pH 7.2 with a wide standard deviation of 2.3 compared to the other two sectors, which was due to an outlier value at one site with a pH of 1.9 as shown in Figure 17. The samples indicated low levels of conductivity, and moderate variation in turbidity across 2 orders of magnitude. Nutrient parameters were lower than the other reported sectors with variances over 1 to 2 orders of magnitude.

Specific parameter by parameter comparisons of each sample are grouped and compared by sector below.
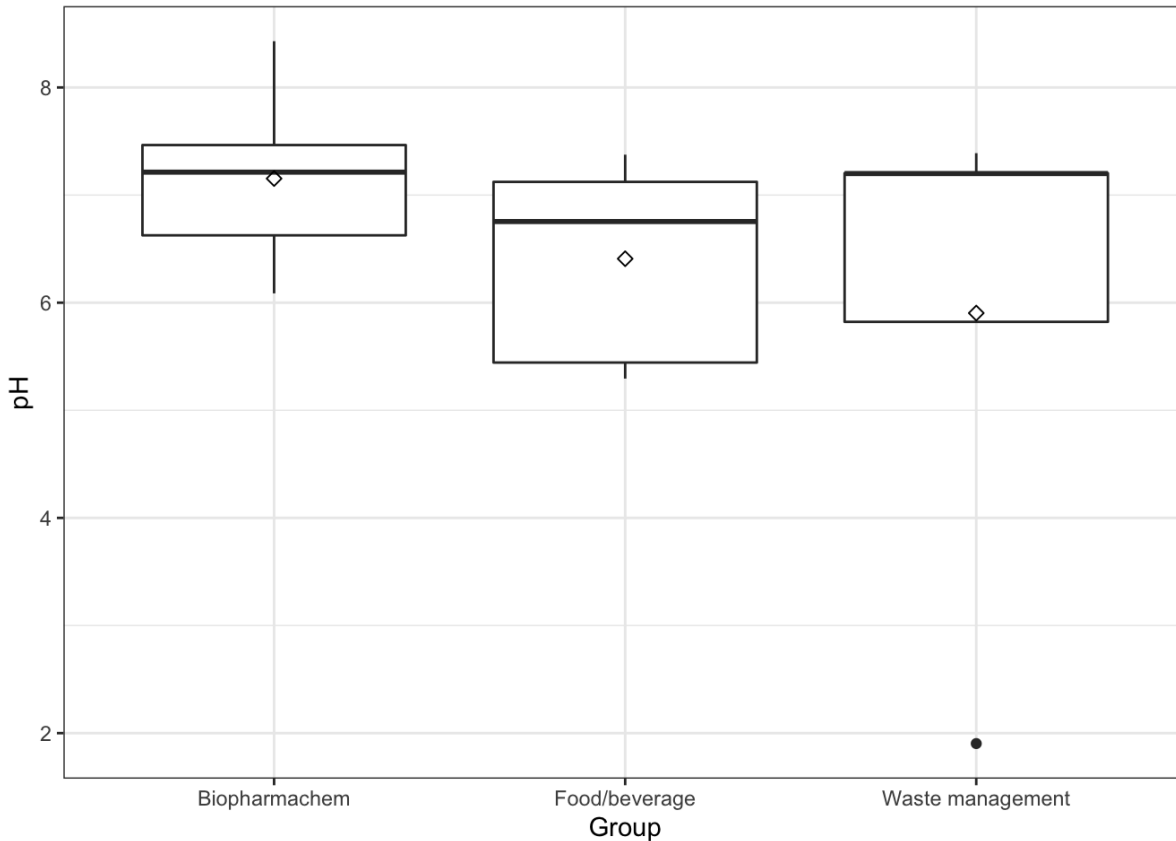
Figure 17 Comparison of pH measurements across the three TE groups. The cross bar indicates the median value, the diamond symbol is the average of all values, and any points are outliers within the dataset

Sample pH (Figure 17) was measured using a glassy pH membrane ion selective electrode that is commonly deployed in-line with TE outlets for real-time monitoring. Comparison of pH measurement indicated that all of the pH values were centred around a mean value of 6.5 ± 1.4, with the food/beverage samples being slightly more acidic (average pH 6.4) compared the biopharmachem group. The average pH value of the waste management sector was strongly impacted by an outlier site with low pH values of 1.9, however the median value was similar to that of the biopharmachem sector at 7.2.
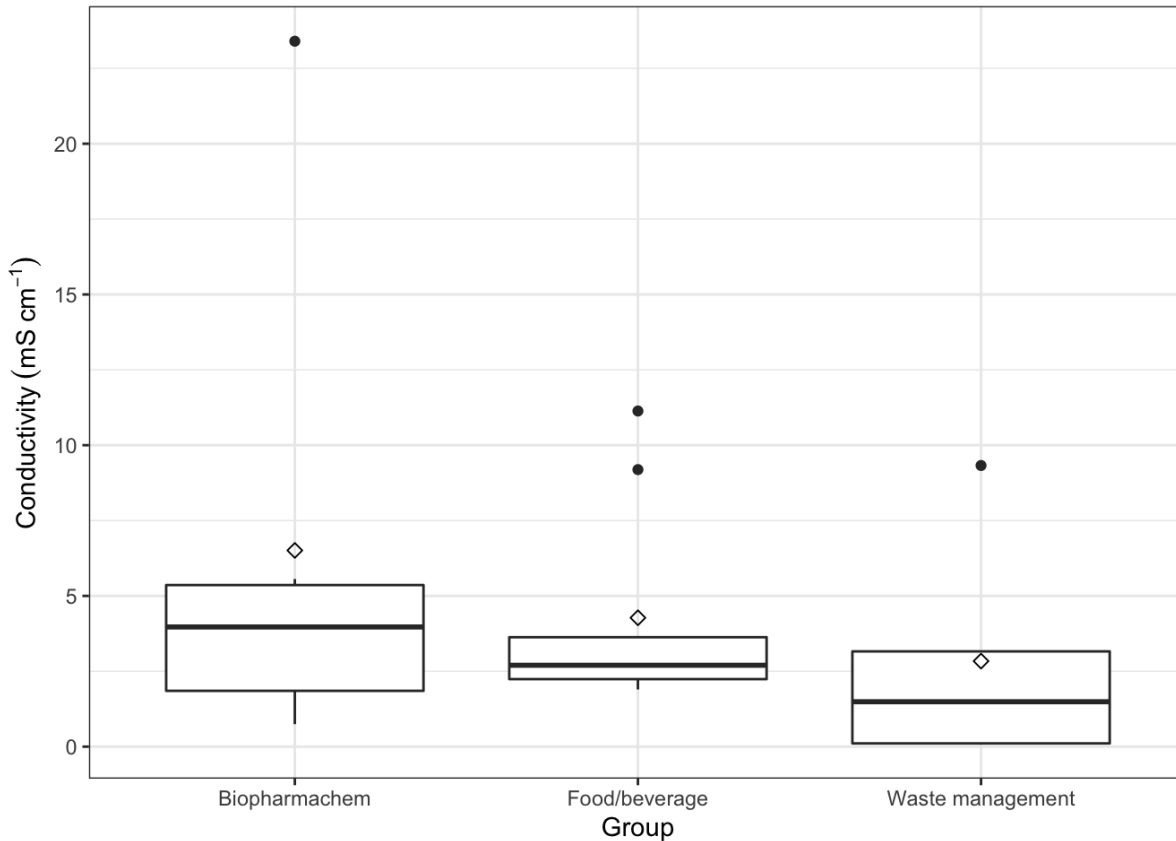
Figure 18 Comparison of conductivity measurements across the three TE groups. The cross bar indicates the median value, the diamond symbol is the average of all values, and any points are outliers within the dataset

The conductivity (Figure 18) of TE samples was measured using a conductivity probe technology that is commonly used for process control within wastewater treatment plants and other industrial processes. Conductivity measurements varied across 3 orders of magnitude from 0.1 to 23.4 mS/cm, with biopharmachem samples offering the widest range of conductivities and the highest average and median values due to the impact of an outlier measurement. TE from the food/beverage sector had slightly lower average conductivities than the biopharmachem sector, however there were similarly two outlier measurements indicated in the dataset. The waste management samples indicated low levels of conductivity (1.5 ± 3.8 mS/cm), while both the biopharmachem and food/beverage sectors were on the order of 8.6 ± 10.1 and 4.4 ± 3.2 mS/cm.
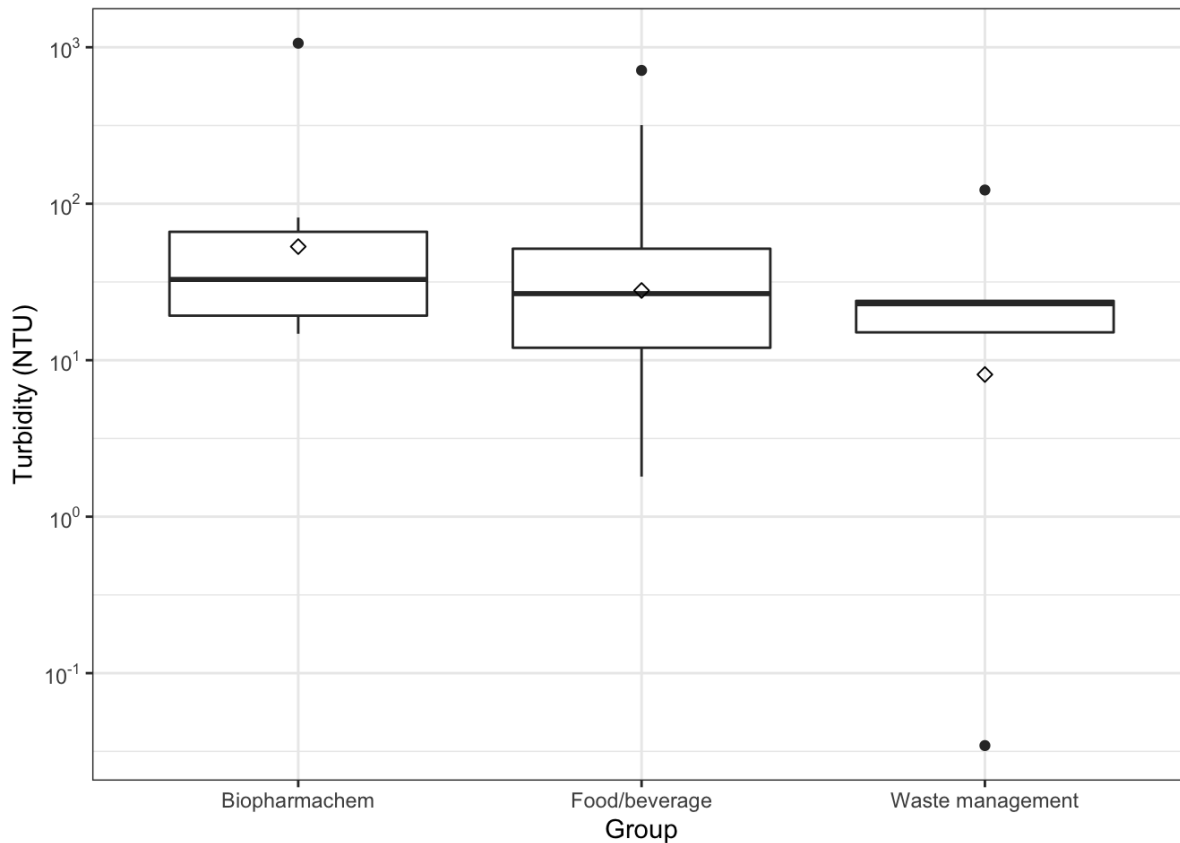
Figure 19 Comparison of measurements of turbidity across the three TE groups. The cross bar indicates the median value, the diamond symbol is the average of all values, and any points are outliers within the dataset

Turbidity (Figure 19) varied across 6 orders of magnitude (0.034 to 1061 NTU), with an overall sector variance of 129 ± 274 NTUs. All sectors showed similar large variances on a site to site basis, with no clear difference between sectors. The biopharmachem and food/beverage industries had mean turbidity values of 293 ± 512 and 200 ± 340 NTUs respectively. The turbidity of TE from the waste management sector was substantially lower with average values of 37 ± 48 NTUs, with one site being a outlier with very low turbidity of 0.034 NTU due to the treatment process applied.
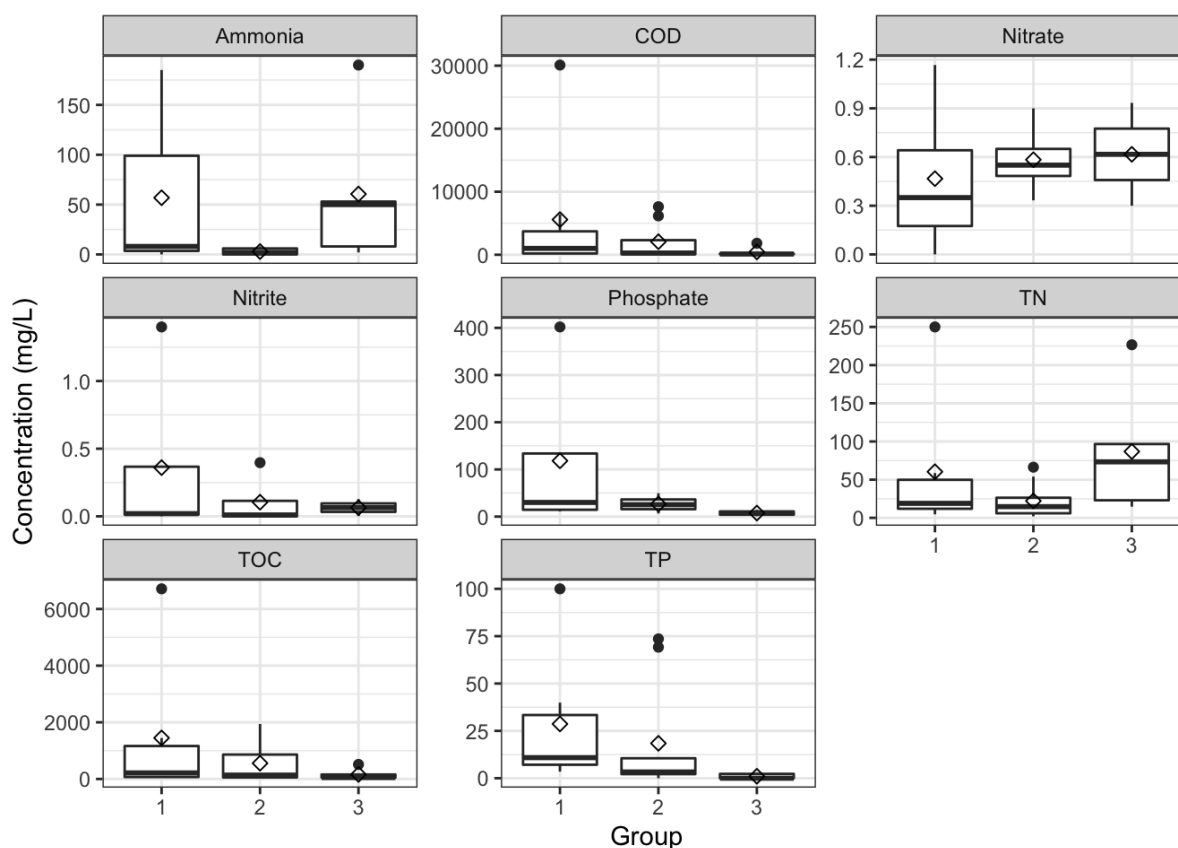
Figure 20 Comparison of wet chemistry measurements across the three TE groups. Group 1 corresponds to the biopharmachem group, 2 is food/beverage, 3 is waste management. The cross bar indicates the median value, the diamond symbol is the average of all values, and any points are outliers within the dataset

Wet chemistry measurements of nutrient and organic parameters for the three sectors is summarised in Figure 20. COD and TOC measurement provide high level information on the amounts of organic species present in TE samples. The average COD concentration of all sites was 2854 ± 6658 mg/L, and COD levels varied over a wide range of 30100 to 51 mg/L. One biopharmachem measurement was a significant outlier in the data set with a COD concentration of 30100 mg/L, however this measurement was typical follow up measurements at the same site. Median values of COD suggest the food/beverage sector (2069 mg/L) typically has higher loadings of organics compared to the biopharmachem (1005 mg/L) and waste management sector (445 mg/L). Average levels of TOC were approximately 30 % of the COD level with an average of 724 ± 1513 mg/L, which is typical of the assay. The TOC measurements indicated similar trends to the COD with biopharmachem and food/beverage sectors having higher levels compared to the waste management sector.

TN revealed that all sectors were outputting TE with similar nitrogen loadings, with one outlier biopharmachem site indicating higher levels of TN on a single occasion. Average levels of TN were 45 ± 80 mg/L with similar median TN levels of 15 to 73 mg/L for all sectors. Similarly, ammonia was measured using a wet chemical assay with colorimetric detection. Ammonia concentrations for all sectors were on average 34.6 mg/L, however this parameter was significantly affected by sporadic higher concentrations of ammonia at some sites, this variability is captured in the wide standard deviations obtained. Median values of ammonia were on average 6 mg/L for all sectors and of 2, 8 and 50 mg/L for the biopharmachem, food/beverage and waste management sectors respectively. One biopharmachem site TE sample was an outlier with a concentration of 190 mg/L however this was not typical of follow up sampling events. The waste management sector typically had the highest levels of ammonia due to the untreated nature of two of the landfill leachate sites that were high in this parameter and TN. Nitrate levels ranged from not detected to 1.2 mg/L in the TE samples, with an average value of 0.54 ± 0.1 mg/L. Nitrite concentrations were slightly lower than the respective concentrations of nitrate with average values of 0.1 ± 0.1 mg/L across all sectors.

TP measurements varied across 2 orders of with average values of 17 ± 21 mg/L, however the median concentration of TP outputted was lower at a level of 3.4 mg/L. The biopharmachem sector indicated the highest average (18 ± 30 mg/L) and median (3.3 mg/L) concentration of TP, followed by the food/beverage sector with an average (29 ± 37 mg/L) and median (30 mg/L). The waste management sector had low levels of TP in all samples (1 ± 1.4 mg/L). The differences between the median and standard deviation of TP levels indicates that this parameter can vary substantially over time on a site to site basis. Phosphate measurements complemented the TP measurements by quantifying the levels of free phosphates TE. There was one outlier measurement within the biopharmachem sector (402 mg/L), however one in this sector indicated similar median phosphate levels of 25 mg/L, compared to the food and beverage sector (30 mg/L), with both groups having significant variability in this parameter. Meanwhile the TE from waste management samples were typically low in phosphates, similar to TP (7.5 ± 9 mg/L).

Ion chromatography

IC was used for the separation and quantitation of inorganic anions in TE samples. Samples were filtered using a 0.45 µm pore size syringe filter prior to separation using IC to prevent blockage of the separation column with particulates. A 10 µL volume of each sample was injected into the instrument, and samples were diluted as required to enable quantitation of anions that exceeded the range of the calibration.

The retention times, repeatability and limits of detection of the five quantitation targets of interest are summarised in Table 16. All retention time repeatability's and limits of detection (LOD) were acceptable for the intended TE monitoring application.

Table 16 IC calibration summary. Retention times reported are the averages of 27 injections of each anion. Calibration range from 0.1 to 100 mg/L of each anion dissolved in deionized water

Anion	Retention time (min)	Retention time RSD (%)	LOD (mg/L)
Chloride	2.729	0.5	0.42
Nitrite	3.215	0.2	0.31
Nitrate	5.344	2.4	0.28
Phosphate	6.869	1.4	0.43
Sulphate	7.967	1.0	0.22

Table 17 summarises the IC results obtained from analysis of TE samples for all groups included in the study.

Table 17 IC results for the biopharmachem, food/beverage and waste management sectors

Group	Measurement	Median	Mean	SD	Max	Min
Biopharmachem	Chloride	588.1	1669.3	2612.2	6951.7	107.2
Biopharmachem	Nitrate	0.5	2.0	3.3	6.9	<LOD
Biopharmachem	Nitrite	<LOD	0.3	0.4	1.0	<LOD
Biopharmachem	Phosphate	20.6	45.0	53.4	112.6	<LOD
Biopharmachem	Sulphate	43.1	44.8	28.9	75.4	<LOD
Food/beverage	Chloride	374.9	956.9	1396.1	4219.4	42.7
Food/beverage	Nitrate	0.3	3.2	4.5	11.7	<LOD
Food/beverage	Nitrite	<LOD	0.9	1.4	2.8	<LOD
Food/beverage	Phosphate	1.5	5.7	6.3	16.0	0.3
Food/beverage	Sulphate	70.0	149.5	160.9	474.7	16.4
Waste management	Chloride	127.2	491.8	728.8	1737.5	0.2
Waste management	Nitrate	1.7	3.0	3.9	8.6	<LOD
Waste management	Nitrite	0.5	3.0	5.4	11.2	<LOD
Waste management	Phosphate	0.8	1.4	1.8	3.8	<LOD
Waste management	Sulphate	89.8	103.6	117.7	301.2	1.4

It is important to note the anion determinations by IC complement the wet chemistry methods discussed above. The analysis techniques differ in that the wet chemistry method does not utilise a filtration step prior to the chemical assay meaning that any nitrate or nitrite that is bound within

particulates can contribute to the colorimetric reaction. In the case of the IC method these particulates are removed before injection to the instrument so only the dissolved fraction is accessible with this method.

A comparison of anions quantified by IC is shown below in Figure 21. Chloride levels were substantially higher than other anions measured by IC, this is due to the ubiquitous presence of chlorides in products and waste. Additionally many of the sites used sodium hydroxide or hydrochloric acid for pH balancing of their effluent prior to release, which will contribute chloride anions to the TE. The mean concentration of chloride for all sectors was 1050 ± 1699 mg/L, with a median of 545 mg/L. Some sites had relatively high levels of chloride compared to others which caused a difference between the median and mean chloride values. Chloride levels were highest in the biopharmachem sector (average 1699 mg/L) likely due to the usage of salt containing buffers and reagents that are required during production. The food/beverage had concentrations of chloride (average 957 mg/L) compared to the waste management group (491 mg/L).
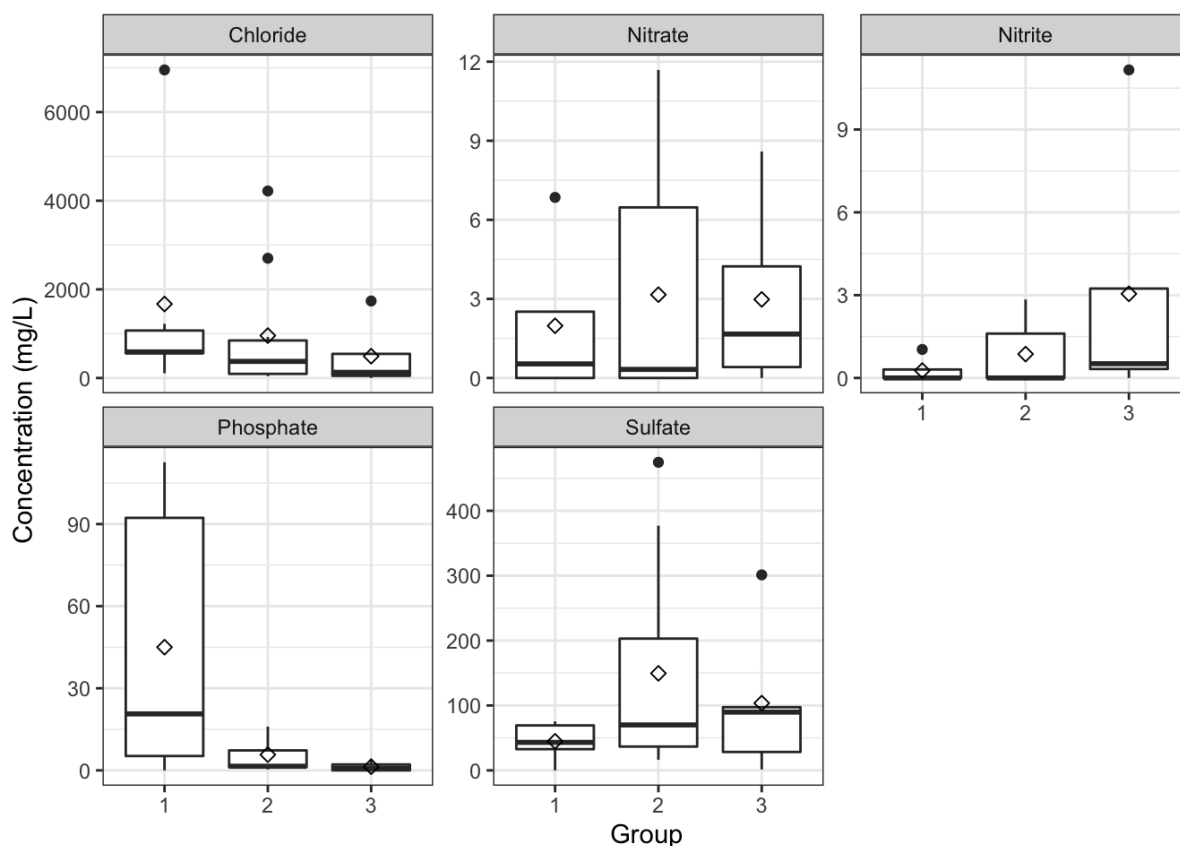
Figure 21 IC results for chloride, nitrate, nitrite, phosphate and sulphate for three industrial groups. Group 1 = biopharmachem, group 2 = food/beverage, group 3 = waste management

Levels of nitrate and nitrite were low across all samples and sectors with median concentrations of 0.4 and 0.2 mg/L respectively. Phosphate concentrations were the highest and most variable within the biopharmachem sector with average concentrations of 45 ± 53 mg/L and a median of 20 mg/L. Phosphate containing buffers and compounds are commonly utilised in the production of pharmaceuticals which could explain the higher levels and large variability detected for this species. Levels of phosphate in the food/beverage (average 6 mg/L) and waste management sectors (2 mg/L) were appreciably lower due to differences in TE composition and TE treatments prior to release. The average concentration of sulphate across all samples was 109 ± 129 mg/L. Sulphate concentrations were highest in the food/beverage sector due as a selection of the sites used sulphuric acid and sulphate containing compounds using during the operation of dissolved air flotation technologies for TE treatment prior to release to sewer. On average and by median the level of sulphate were higher in the waste management while the biopharmachem sector indicated the lowest levels of sulphate.

IC provided a rapid method (15 min separation time for each sample) for quantifying anions in TE samples with minimal requirements for sample preparation (filtration and dilution only). There was broad agreement between wet chemistry and IC measurements of anions, although concentrations determined by IC were sometimes lower than wet chemistry measurements due to the elimination of interferences provided by the separation column prior to conductivity detection.

Organics analysis

The analysis of organic compounds was carried out using GC coupled with MS. This technique provided the capacity to separate and identify a quantitate wide variety of organic compounds in TE. Prior to analysis of the TE samples by GC-MS, a sample preparation step was required to remove large particles that would contaminate the GC-MS and change the solvent from water to a volatile organic solvent compatible with the instrument. For the present work a 0.7 µm pore size filter was selected to allow filtration to be completed in a timely manner, and the water solvent was exchanged for dichloromethane during the SPE procedure below which prevents degradation of the GC separation column and stabilises organic compounds against hydrolysis during storage and analysis.

A volume of 100 mL was selected for filtration and extraction using an Oasis HLB solid phase extraction cartridge which is able to concentrate and adsorb organics from this volume of water and then release them using an organic solvent. The Oasis HLB SPE cartridge is a general purpose device that allows the extraction of polar and non-polar compounds from water samples

and it has been utilized in a wide variety of water related studies (Andrade-Eiroa et al., 2016a, 2016b; Robles-Molina et al., 2014) and is recommended by for use by the EPA 8270 method for measuring semivolatiles in water and waste water samples (US EPA, 2019). Dichloromethane was used as the elution solvent as this solvent able to elute strongly retained organics from the SPE cartridge and the solvent can easily be evaporated to concentrate the organics into a small volume.

A test mixture was selected that contained a wide variety of organic compounds including, phenols, aromatic hydrocarbons, polyaromatic hydrocarbons, anilines, nitrobenzenes, phthalates and alcohols that are potentially of interest for monitoring in TE. This mixture included 76 components to facilitate identification and quantification, along with an additional set of 6 internal and surrogate standard compounds. The list of compounds includes a selection of targets that are commonly analysed using the EPA Method 8270 for semi-volatile organics analysis that can impact the quality of water samples (US EPA, 2019). A mixture of linear n-alkanes from n-heptane (C_7) to n-triacontane (C_{30}) for a total of 26 n-alkanes were also analysed for retention time marking and peak identification purposes. An example of the separation of the test mixture selected is shown in Figure 22 and the identities of each peak are shown in Table 18.
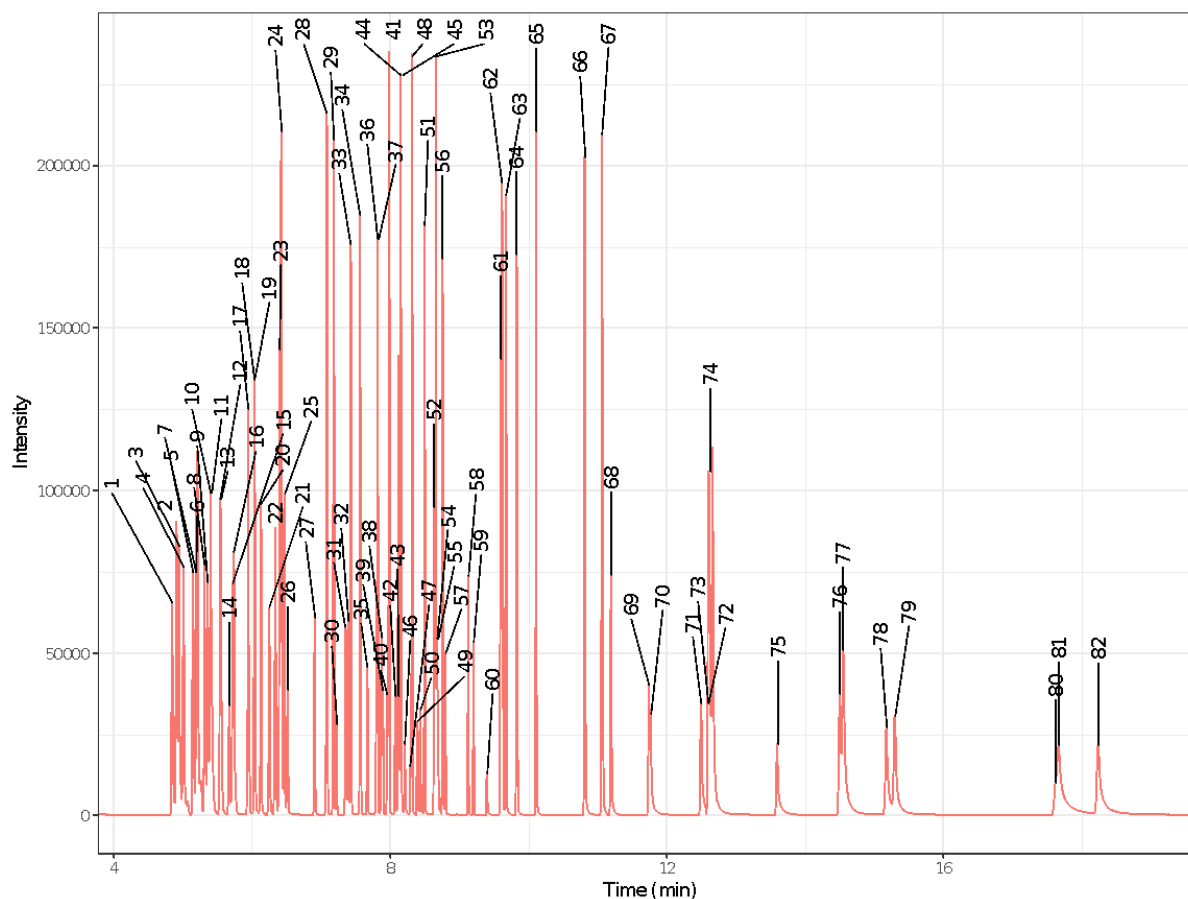
Figure 22 GC-MS separation of organics test mixture. See Table 18 for peak compound identification

Some components of the test mixture were not completely separated, for example peaks 80 and 81, however mass spectrometry provides the capacity to detect one compound in the presence of another by searching for ions characteristic of the target compounds. Table 18 details the characteristic ions (*m/z* values) used for identification and quantification of target compounds at each retention time.

Table 18 List of peak numbers, compound names, chemical abstract service (CAS) identifier numbers and the retention time in the organics test mixture. Two ions (1 and 2) are used for the identification and quantification of each compound. The Internal standards (IS) and recovery check compounds (REC) are indicated in the note column

Peak #	Compound name	CAS #	Retention time (min)	Ion 1 (m/z)	Ion 2 (m/z)	Note
1	Phenol	108-95-2	4.850	94	66	
2	Aniline	62-53-3	4.916	93	66	
3	Bis(2-Chloroethyl)ether	111-44-4	4.952	93	63	

4	2-Chlorophenol	95.57-8	5.013	128	64	
5	1,3-Dichlorobenzene	541-73-1	5.151	146	148	
6	1,4-Dichlorobenzene-d_4	3855-82-1	5.200	152	150	IS
7	1,4-Dichlorobenzene	106-46-7	5.200	146	148	
8	Benzyl alcohol	100-51-6	5.325	108	79	
9	1,2-Dichlorobenzene	95-50-1	5.367	146	148	
10	2-Methylphenol	95-48-7	5.405	107	108	
11	2,2'Oxybis(1-chloropropane)	108-60-1	5.430	121	123	
12	3-Methylphenol (coelution)	108-39-4	5.546	107	108	
	4-Methylphenol (coelution)	106-44-5	5.546	107	108	
13	*N*-Nitroso-di-n-propylamine	621-64-7	5.563	107	108	
14	Hexachloroethane	67-72-1	5.677	130	70	
15	Nitrobenzene-d_5	4165-60-0	5.729	117	201	REC
16	Nitrobenzene	98-95-3	5.744	82	128	
17	Isophorone	78-59-1	5.952	77	123	
18	2-Nitrophenol	88-75-5	6.045	82	138	
19	2,4-Dimethylphenol	105-67-9	6.045	139	109	
20	Bis(2-chloroethoxy)methane	111-91-1	6.138	122	107	
21	2,4-Dichlorophenol	120-83-2	6.256	93	95	
22	1,2,4-trichlorobenzene	120-82-1	6.342	162	164	
23	Naphthalene-d_8	1146-65-2	6.409	180	182	IS
24	Naphthalene	91-20-3	6.428	136	68	
25	4-Chloroaniline	106-47-8	6.472	128	129	
26	Hexachlorobutadiene	87-68-3	6.520	127	129	
27	4-Chloro-3-methylphenol	59-50-7	6.912	225	223	
28	2-Methylnaphthalene	91-57-6	7.088	107	144	
29	1-Methylnaphthalene	90-12-0	7.188	142	141	
30	Hexachlorocyclopentadiene	77-47-4	7.231	142	141	
31	2,4,6-Trichlorophenol	88-06-2	7.359	235	237	
32	2,4,5-Trichlorophenol	95-95-4	7.394	196	198	
33	2-Fluoro-biphenyl	321-60-8	7.434	196	198	REC
34	2-Chloronaphthalene	91-58-7	7.573	172	171	
35	2-Nitroaniline	88-74-4	7.673	162	127	
36	1,4-Dinitrobenzene	100-25-4	7.819	65	92	
37	Dimethyl phthalate	131-11-3	7.83	168	75	
38	1,3-Dinitrobenzene	99-65-0	7.879	163	194	
39	2,6-Dinitrotoluene	606-20-2	7.900	168	76	
40	1,2-Dinitrobenzene	528-29-0	7.964	165	50	
41	Acenaphthylene	208-96-8	7.988	168	50	
42	3-Nitroaniline	99-09-2	8.078	152	151	
43	Acenaphthene-d_{10}	15067-26-2	8.124	138	108	IS
44	Acenaphthene	83-32-9	8.157	164	162	
45	2,4-Dinitrophenol	51-28-5	8.178	154	153	
46	4-Nitrophenol	100-02-7	8.217	184	63	

47	2,4-Dinitrotoluene	121-14-2	8.297	139	109	
48	Dibenzofuran	132-64-9	8.322	165	63	
49	2,3,4,6-tetrachlorophenol	58-90-2	8.395	168	139	
50	2,3,5,6-tetrachlorophenol	935-95-5	8.438	232	131	
51	Diethyl phthalate	84-66-2	8.503	232	131	
52	4-chlorophenyl phenyl ether	7005-72-3	8.642	149	177	
53	Fluorene	86-73-7	8.660	204	206	
54	4-nitroaniline	100-014-6	8.685	166	165	
55	4,6-dinitro-2-methylphenol	534-52-1	8.700	138	65	
56	Diphenylamine	122-39-4	8.763	198	105	
57	Azobenzene	103-33-3	8.801	169	168	
58	4-bromophenyl phenyl ether	101-55-3	9.131	182	152	
59	Hexachlorobenzene	118-74-1	9.210	248	250	
60	Pentachlorophenol	87-86-5	9.403	284	142	
61	Phenanthrene-d_{10}	1517-22-2	9.606	266	264	IS
62	Phenanthrene	85-01-8	9.625	188	94	
63	Anthracene	120-12-7	9.677	178	179	
64	Carbazole	86-74-8	9.835	178	179	
65	Di-*n*-butylphthalate	84-74-2	10.11	167	166	
66	Fluoranthene	206-44-0	10.819	149	150	
67	Pyrene	129-00-0	11.069	202	101	
68	*p*-Terphenyl-d_{14}	1718-51-0	11.197	202	200	REC
69	Benzyl butyl phthalate	85-68-7	11.744	244	122	
70	Bis(2-ethylhexyl)adipate	103-23-1	11.768	149	206	
71	Bis(2-ethylhexyl)phthalate	117-81-7	12.499	147	129	
72	Benz(*a*)anthracene	56-55-3	12.606	149	167	
73	Chrysene	1719-03-5	12.606	228	229	
74	Chrysene-d_{12}	218-01-9	12.630	240	120	
75	Di-*n*-octyl phthalate	117-84-0	13.608	228	226	
76	Benzo(*b*)fluoranthene	205-99-2	14.502	149	167	
77	Benzo(*k*)fluoranthene	207-08-9	14.555	252	253	
78	Benzo(*a*)pyrene	50-32-8	15.177	252	253	
79	Perylene-d_{12}	1520-96-3	15.309	252	253	IS
80	Indeno(1,2,3-*cd*)pyrene	193-39-5	17.631	264	260	
81	Dibenz(*a,h*)anthracene	53-70-3	17.668	276	138	
82	Benzo(*g,h,i*)perylene	191-24-2	18.242	278	139	IS

The GC-MS separations of extracted organics from each of the 15 sites included in the study are shown below.
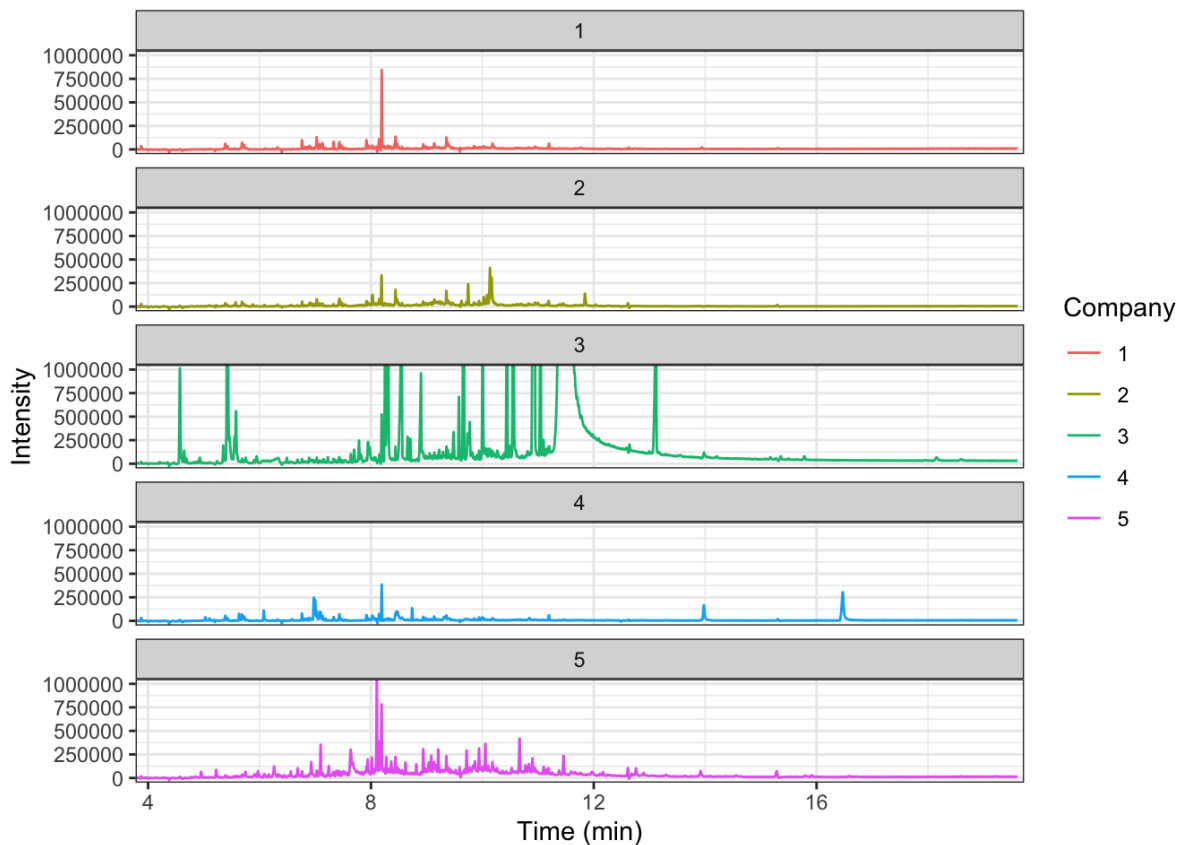
Figure 23 GC-MS separation showing the total ion chromatograms of TE from five biopharmachem companies. The number of peaks detected in each chromatogram for the companies are: Company 1 – 164, Company 2 – 179, Company 3 – 160, Company 4 – 160 and Company 5 – 234 peaks

Analysis of the biopharmachem TE group (Figure 23) revealed that the number of compounds and total levels of organic compounds detected in biopharmaceutical derived TE (Companies 1, 2, 4) was lower than the levels of organics found in companies that are producing small molecule synthetic drugs (Companies 3 and 5).
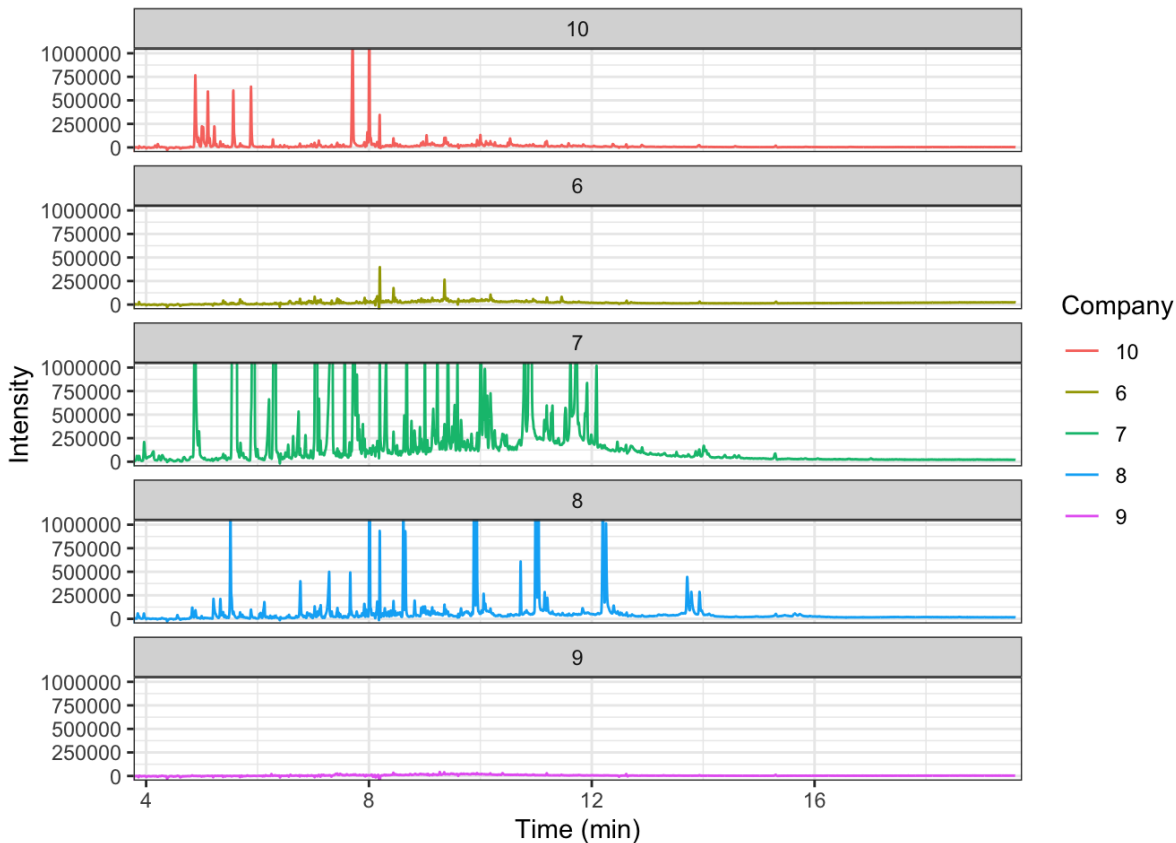
Figure 24 GC-MS separation showing the total ion chromatograms of TE from five food/beverage companies. The number of peaks detected in each chromatogram for the companies are: Company 6 –166, Company 7 – 230, Company 8 – 230, Company 9 – 158, Company 10 - 187 peaks

In the case of the food/ beverage companies, five different profiles were obtained for each TE source with indications of both high and low levels of organic compounds. Site 6 was primarily processing food products, and a limited number of organics were detected, however it is important to note that this extraction method focuses on the extraction of chemical species such as drugs and organic solvents instead of proteins and biomolecules that are more common in foods or biopharmaceuticals. Site was producing a range of alcoholic and non-alcoholic beverages which manifested large numbers of organic species following the SPE extraction technique employed. Site 8 and 10 were producing dairy products and each site had significant variation in the amounts of organics detected due to differences in production and TE treatment. Finally site 9 was producing non-alcoholic beverages, however its TE treatment system appears to be highly effective at eliminating organics.
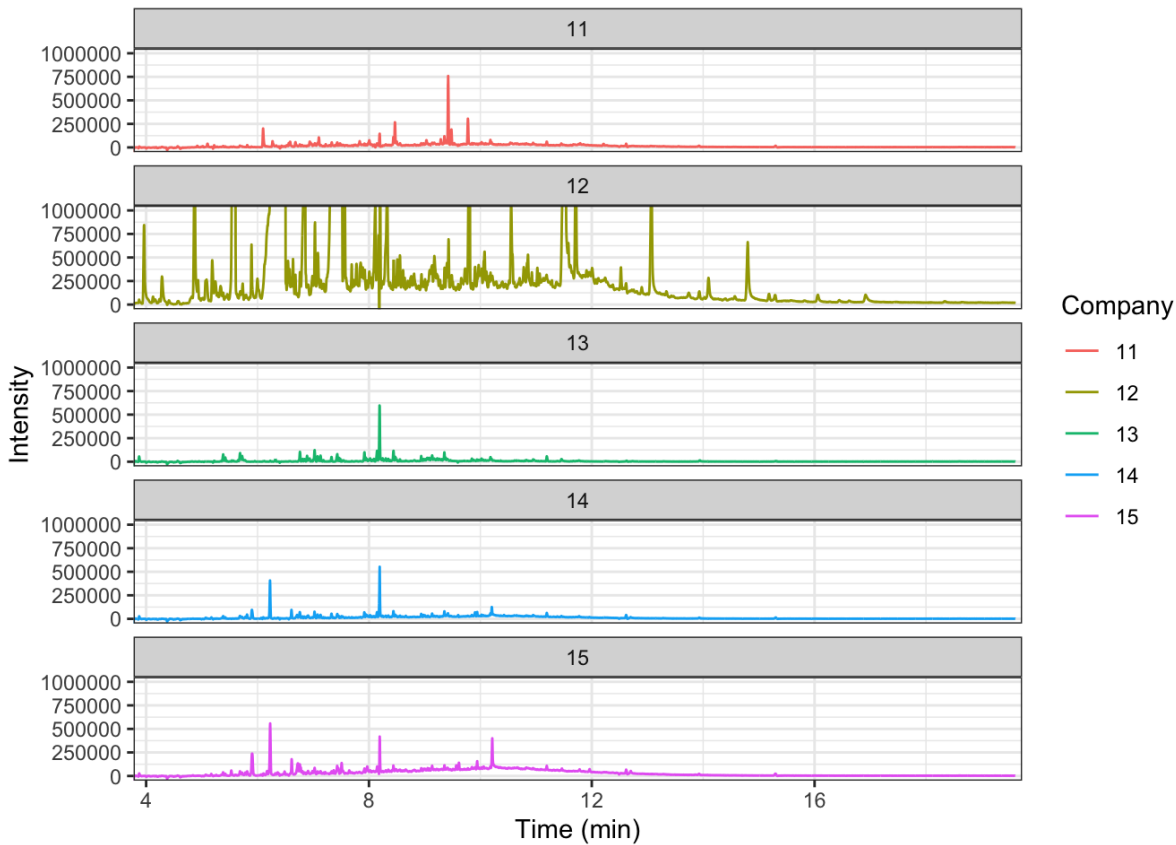
Figure 25 GC-MS separation showing the total ion chromatograms of TE from five food/beverage companies. The number of peaks detected in each chromatogram for the companies are: C11 – 193, C12 – 209, C13 – 156, C14 – 175, C15 – 191 peaks

Overall levels of organics detected in the water management companies were relatively low, with the exception of site 12 which was an untreated landfill leachate sample. Samples 11 and 13 were obtained from companies carrying out recycling and organic processing operations. Site 14 and 15 were obtained from landfill leachates, with varying levels of TE treatment.

Analysis and identification of specific organics was performed using mass spectral data and selective ion monitoring was used to quantify levels of targeted organic compounds. Figure 26 summarises the levels of organic compounds that were identified and quantitated within TE samples obtained from the company classes.
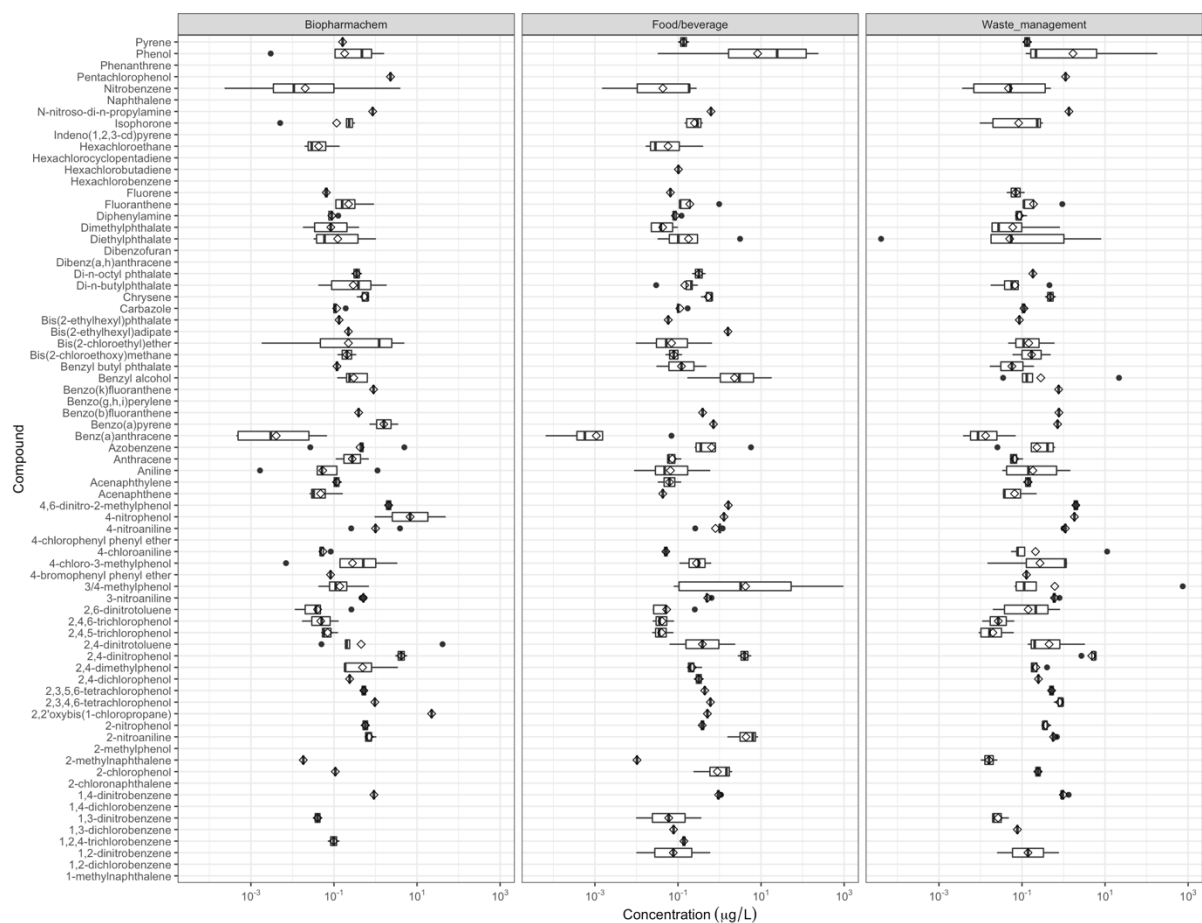
Figure 26 Summary of organic species found to be present in each of the three TE sectors evaluated: biopharmachem, food/beverage and waste management

The data indicate that individual organics are usually present in concentrations below 1 µg/L. There are some compounds that present at higher levels of approximately 10 ug/L including phenol, 3/4-methylphenol, benzyl alcohol, some nitrophenols and diethyl phthalate. Levels of polycyclic aromatic hydrocarbons were around the 1 µg/L range, while other phthalates and phenol derivatives were between not detected and 0.5 µg/L depending on the sample.

Analysis of biopharmachem organics indicates that the levels of most individual species were below the level of 1 µg/L, with exceptions of 2,2'oxybis(1-chloropropane), 4-chloro-3-methylphenol, 4-nitrianiline, 4-nitrophenol, 4,6-dinitro-2-methylphenol, azobenzene, benzo(a)pyrene, di-*n*-butyl phthalate, nitrobenzene, pentachlorophenol and phenol. Out of these compounds the phenol and benzyl classed compounds stand out as interesting surrogate targets due to the potential to measure these compounds with sensors. Food/beverage TE exhibited similarly low levels (< 1 µg/L) of most individual organic chemicals. Compounds with concentrations greater than 1 µg/L included 2-chlorophenol, 2,4-chlorophenol, 2,4-dinitrotoluene,

3/4-methylphenol 4,6-dinitro-2-methylphenol, azobenzene, benzyl alcohol, bis(2-ethylhexyl)adipate, diethyl phthalate and phenol. Variation in phenols and benzyl alcohol may be useful for speciation of TE. Finally, organics in TE samples from the waste management sector showed elevated levels of 2,4-dinitrophenol, 3/4-methylphenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, aniline, benzyl alcohol, diethyl phthalate and phenol. While the remaining target compounds were either absent or present at levels below (1 µg/L). These compound classes can potentially be detected using spectroscopic, electrochemical and fluorescence techniques. Correlation of organic compounds with parameters such as COD could be valuable for establishing monitoring techniques for these species (Chen et al., 2014; Geerdink et al., 2017).

Metals and inorganics

TE samples were analysed for a selection of light and heavy metals along with additional inorganic species using ICP-OES (see Table 9). Samples were digested at high temperature (100 °C) using concentrated nitric acid to obtain the total levels of insoluble, particulate bound and soluble metals. Average levels of the target metals are compared for each of the three TE classes in Figure 27. A number of species were not detected at levels above the detection limits of the present ICP-OES method including silver, arsenic, barium, beryllium, bismuth, cadmium, cobalt, chromium, gallium, indium, lithium, nickel, lead, rubidium, selenium and tellurium.
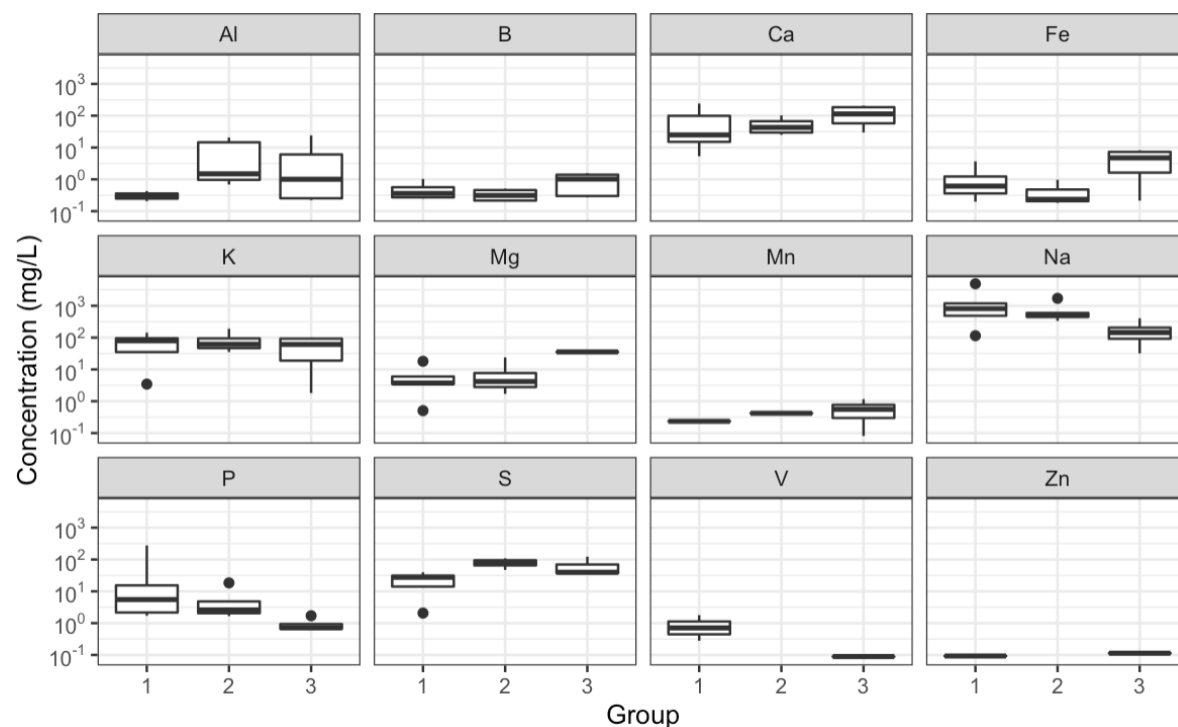
Figure 27 ICP-OES measurement of target metals in TE derived three industrial sectors. Group 1 = biopharmachem, group 2 = food/beverage and group 3 = waste management

Sodium levels were the highest in concentration out of all the metals monitored across all three sectors (average concentrations of 800 ± 1200 mg/L), followed by potassium, calcium, magnesium and sulphur which were approximately ten times lower in concentration compared to sodium. Phosphorous, aluminium and iron were present at levels between 1 and 10 mg/L, and low levels of boron (approximately 1 mg/L) were found in all samples. No substantial amounts of heavy metals, other than aluminium and iron, were detected in the TE samples, with detection limits for the method being 0.1 mg/L on average.

There were some notable differences between inorganic element and metal levels in different TE groups. For example, levels of aluminium were approximately 50 times higher in the food/beverage and waste management categories (averages 8 and 6 mg/L) compared to the biopharmachem sector (average < 1 mg/L). This is likely due to the use of aluminium compounds during dissolved air flotation treatment. The levels of calcium varied from less than 0.1 mg/L to 240 mg/L (average 72 ± 80 mg/L). Iron was present at low levels (maximum 8 mg/L, average 3 mg/L) in all samples, however the levels in waste management samples were 5 times higher than biopharmachem and food/beverage TE. Magnesium levels were approximately 10 ± 9.3 mg/L, with the waste management sector having lower concentrations compared to other sectors. Manganese was detected infrequently at concentrations lower than 1 mg/L, with an average of 0.2 mg/L and similar variation for all sites.

Levels of sodium were higher in the biopharmachem (average 800 mg/L) and food/beverage sector (average 720 mg/L) compared to waste management samples (average 180 mg/L). Phosphorous levels were the highest in biopharmachem derived samples (average 60 mg/L), while food/beverage and waste management samples indicated much lower levels (averages of 5 and 1 mg/L respectively). Levels of sulphur were higher in food/beverage and waste management samples at 63 and 40 mg/L compared to the 20 mg/L levels found in biopharmachem samples. Table 19 summarises the variation in levels of metals measured in TE from the biopharmachem sector.

Table 19 Summary data of ICP-OES measurements for TE samples from the biopharmachem group

Measurement	Median	Mean	SD	Max	Min
Ag	ND	-	-	-	-
Al	0.32	0.32	0.16	0.43	0.21
As	ND	-	-	-	-
B	0.37	0.51	0.36	1.03	0.25
Ba	ND	-	-	-	-
Be	ND	-	-	-	-
Bi	ND	-	-	-	-
Ca	24.97	77.22	99.05	241.55	5.32
Cd	ND	-	-	-	-
Co	ND	-	-	-	-
Cr	ND	-	-	-	-
Cu	0.55	0.55	NA	0.55	0.55
Fe	0.65	1.30	1.62	3.69	0.20
Ga	ND	-	-	-	-
In	ND	-	-	-	-
K	79.56	76.50	57.32	143.43	3.45
Li	ND	-	-	-	-
Mg	3.73	6.35	6.81	18.03	0.51
Mn	0.23	0.23	NA	0.23	0.23
Na	815.34	1506.60	1952.29	4925.66	114.69
Ni	ND	-	-	-	-
P	5.51	60.14	120.78	275.98	1.71
Pb	ND	-	-	-	-
Rb	ND	-	-	-	-
S	27.59	24.22	15.84	39.64	2.07
Se	ND	-	-	-	-
Sr	0.45	0.45	NA	0.45	0.45
Te	ND	-	-	-	-
V	1.04	1.04	1.07	1.79	0.28
Zn	0.09	0.09	NA	0.09	0.09

Table 20 summarises the variation in levels of metals measured in TE from the food/beverage sector.

Table 20 Summary data of ICP-OES measurements for TE samples from the food/beverage group

Measurement	Median	Mean	SD	Max	Min
Ag	ND	-	-	-	-
Al	1.49	7.68	9.34	20.66	0.69
As	ND	-	-	-	-
B	0.33	0.34	0.16	0.51	0.20
Ba	ND	-	-	-	-
Be	ND	-	-	-	-
Bi	ND	-	-	-	-
Ca	44.85	54.41	35.46	102.97	24.98
Cd	ND	-	-	-	-
Co	ND	-	-	-	-
Cr	ND	-	-	-	-
Cu	ND	-	-	-	-
Fe	0.24	0.46	0.44	0.97	0.18
Ga	ND	-	-	-	-
In	ND	-	-	-	-
K	62.85	87.96	70.37	190.76	35.39
Li	ND	-	-	-	-
Mg	4.28	8.53	10.32	23.85	1.70
Mn	0.42	0.42	NA	0.42	0.42
Na	493.61	717.38	564.28	1712.82	335.06
Ni	ND	-	-	-	-
P	2.64	6.34	8.07	18.41	1.67
Pb	ND	-	-	-	-
Rb	ND	-	-	-	-
S	81.39	79.81	26.47	109.42	47.06
Se	ND	-	-	-	-
Sr	ND	-	-	-	-
Te	ND	-	-	-	-
V	ND	-	-	-	-
Zn	ND	-	-	-	-

Table 21 summarises the variation in levels of metals measured in TE from the waste management sector.

Table 21 Summary data of ICP-OES measurements for TE samples from the waste management group

Measurement	Median	Mean	SD	Max	Min
Ag	ND	-	-	-	-
Al	2.05	7.10	11.44	24.08	0.22
As	ND	-	-	-	-
B	1.02	0.91	0.61	1.58	0.27
Ba	ND	-	-	-	-
Be	ND	-	-	-	-
Bi	ND	-	-	-	-
Ca	125.38	121.74	84.37	206.42	29.78
Cd	ND	-	-	-	-
Co	ND	-	-	-	-
Cr	ND	-	-	-	-
Cu	ND	-	-	-	-
Fe	5.11	4.64	3.63	8.14	0.21
Ga	ND	-	-	-	-
In	ND	-	-	-	-
K	65.95	58.38	45.64	99.83	1.80
Li	ND	-	-	-	-
Mg	35.46	35.46	NA	35.46	35.46
Mn	0.57	0.60	0.45	1.17	0.08
Na	144.62	176.12	143.56	405.69	31.83
Ni	ND	-	-	-	-
P	0.72	0.94	0.51	1.71	0.63
Pb	ND	-	-	-	-
Rb	ND	-	-	-	-
S	39.64	65.89	49.37	122.83	35.20
Se	ND	-	-	-	-
Sr	0.81	0.81	0.20	0.95	0.66
Te	ND	-	-	-	-
V	0.09	0.09	NA	0.09	0.09
Zn	0.11	0.11	NA	0.11	0.11

Conclusions

The aim of this section was to characterise the wastewater samples from each trade using organoleptic wet chemistry, organics and inorganics analysis techniques. The data obtained from this chemical characterisation sought to identify the levels of commonly monitored species within TE to determine which targets may be of interest sensor or passive sampling monitoring. The levels and variation of COD, TOC, nutrients and ionic species indicate that the organic and inorganic components of TE are present at levels amenable to sensor, spectroscopic and passive sampling monitoring. Furthermore, testing with conductivity and turbidity sensors indicate that these commercially available sensors are able to detect bulk differences in the properties of TE samples that may provide insight into changes in TE composition. While conductivity and turbidity measurements have low selectivity for specific targets such as COD or ammonia, knowledge about the composition of specific sectors or sites is important for correlating changes in these sensors with specific monitored parameters. Commercial sensors for ammonia, nitrite, and nitrate are available and ammonia sensors are of particular interest due to the variation that this species shows in the biopharmachem, food/beverage and waste management sectors.

3

Evaluation of industrial inputs to sewer networks

Evaluation of industrial inputs to sewer networks

Introduction

The primary goals of TE management are to maintain sewer network integrity, to minimise the impact of TE to the environment and to reduce impacts on the operation of downstream wastewater treatment plant (WWTP) infrastructure. While WWTPs are well optimised for the treatment of urban and commercial wastewater, industrial TE can present challenges due to its differences in composition compared to urban/commercial waste and its variability in properties over time. While the concentration of various organic, inorganic and metallic species provides valuable information on the composition of TE, it is important to consider mass loadings of these species that are emitted to sewer networks. Large volumes of low concentration TE can have similarly deleterious impacts on downstream wastewater treatment plant infrastructure as lower volume high concentration TE. This section investigates the TE outputs of the biopharmachem, food/beverage and waste management sectors in Ireland. Additionally, rainfall was investigated as a potential parameter that could affect overall outputs and dilution of TE.

Industrial TE management focuses on limiting the emission of important species into sewer networks based on threshold values using removal strategies such as filtration, sedimentation, precipitation, biochemical degradation, coagulation and dissolved air flotation among other techniques (Deegan et al., 2011; Gadipelly et al., 2014; Mai et al., 2018). While removal strategies have been utilised effectively in industry for some time, there is an increasing amount of interest in investigating methods of recovering and reusing components from TE for purposes of promoting sustainability and the development of a circular resource economy (Solon et al., 2019; Mavhungu et al., 2020; Sfez et al., 2019). In addition to promoting sustainable resource usage, recovery strategies have potential benefits enhancing water quality and providing additional revenue streams to offset some of the costs of TE management. Both removal and recovery TE treatment strategies reduce levels of licensed parameters in industrial TE to improve compliance with emissions limits which has reduces operational burdens on downstream WWTP infrastructure.

A variety of chemical species have been explored for recovery opportunities, however the most promising targets are nutrients, energy from biogas generation and selected valuable metals/organic species (Solon et al., 2019). Some industries employ methods to recover metals and organic chemicals that are used in site processes to recycle material and reduce costs while ensuring that TE parameters are maintained within licensed limits. Recovery of materials from TE is achieved using a wide variety physicochemical processes such as adsorption, precipitation,

membrane filtration; biological approaches using bacterial degradation or bioconcentration; or with electrochemical techniques including electrodeposition, electrocoagulation or flocculation (Arashiro et al., 2018; Golnaraghi Ghomi et al., 2020; Jin and Zhang, 2020).

Phosphorous (P) is an essential nutrient for biological growth that is incorporated into fertilisers in agriculture, as well as being used in commercial products and as a material or reagent during production. The release of phosphorous to natural environments is implicated with growth of blue-green algae, which can trigger eutrophication and death of flora and fauna in water bodies (Worsfold et al., 2016). Furthermore phosphorous has been identified as a diminishing natural resource requiring careful management to ensure access to this nutrient for agriculture (Desmidt et al., 2015). For these reasons, phosphorous release is controlled using an array of removal technologies including sedimentation and filtration of particulate bound phosphate coupled with bacterial removal strategies prior to TE release. There are two primary methods for extracting phosphorous/phosphates from TE or wastewater, the chemical precipitation or adsorption methods (Egle et al., 2015). Out of the two strategies the precipitation method is often more favoured due to the ability to separate the precipitated phosphate material from water using filtration (Chen et al., 2009). P is often precipitated from solution using either magnesium to form struvite or using calcium to form hydroxyapatite (Desmidt et al., 2015). The requirement of desorption of phosphates from adsorption materials presents an additional step, although this method does have the benefit of providing a regenerated adsorption material that can be reused in follow-up recoveries (Ye et al., 2017). P recovery can also be performed on sludge TE streams that are commonly generated by dissolved air flotation, filtration and sedimentation techniques coupled with biological treatments utilised within industry and municipal waste water treatment plants. Recovery of phosphorous from TE has been identified as a potentially valuable strategy given the increasing rarity of this essential nutrient for agriculture (Loganathan et al., 2014).

Nitrogen containing species are another important component of TE that are present in the form of organically bound nitrogen, ammonia, nitrate and nitrite species. Similar to phosphate, excess nitrogen containing species can impact water quality and affect the treatment of TE at wastewater treatment plants (Beckinghausen et al., 2020). Nitrogen is an essential nutrient utilised as a fertiliser component in agriculture, usually in the form of urea or ammonia salts such as ammonium nitrate or ammonium sulphate. The bulk of ammonia produced for fertiliser is generated through the Haber-Bosch process which uses catalysis to convert diatomic nitrogen into ammonia using hydrogen gas (Beckinghausen et al., 2020). This process is heavily dependent on fossil fuels for a supply of hydrogen gas that is generated through steam reformation. Nitrogen removal is currently performed using aeration and biological reactors that

perform nitrification and denitrification to reduce levels of TN and ammonia in their TE. However, this conversion back to atmospheric nitrogen is a significant loss considering the large energy expenditure required to fix nitrogen and synthesise fertilisers. Therefore the recovery of nitrogen from TE and wastewater presents an important opportunity for the development of circular economies. Nitrogen recovery can be achieved through a range of processes. Physical processes that allow the extraction of nitrogen in the form of ammonia include membrane processes (M. Xie et al., 2016), filtration (Gerardo et al., 2013), adsorption and gas stripping (Ukwuani and Tao, 2016). Nitrogen in the form of ammonium can also recovered with phosphate during struvite generation (Kataki et al., 2016; Perera et al., 2019).

In addition to nutrient recovery of phosphorous and nitrogen, some companies implement specifically tailored resource recovery technologies in their production and TE treatment processes to recycle expensive materials such as solvents, catalysts organic reagents (Chea et al., 2020; Shores et al., 2020). Such opportunities are highly dependent on the nature of operations being carried out at a given industrial site, for example solvent recovery is commonly performed on pharmaceutical TE as these solvents are often environmentally hazardous and costly to replace (Gadipelly et al., 2014). In this section the loadings of organics, inorganics, nutrients and metals were calculated based on annual and daily outputs of TE from 15 companies. This process was used to inform the amounts of these species that are potentially available for recovery.

Methods

Wet chemistry, organics and metals analysis was performed on all samples as described in Section 3. Daily flow rates and annual emission volumes were obtained from Annual Environmental Reports and company supplied supplementary information. Companies are required to produce Annual Environmental Reports (AERs) as a component of their emissions licences granted by the EPA and these reports are published to the EPA website. Irish Water also requires some larger companies to submit emissions reports for the industry licences managed by themselves. Annual emissions volumes were averaged over the 2015 to 2019 period to provide company and then sector averaged emissions levels typical of each of the three industrial groups assessed. A summary of the companies contributing data to this report and the data sources used is provided in Table 22.

Table 22 Summary of TE emissions data available for companies included in this project. Group 1 = Biopharmachem, Group 2 = Food/beverage, Group 3 = Waste management/Landfill. Weather stations were selected based on proximity to each

industrial site, some weather stations were in close proximity with multiple sites. *An additional company was added to the dataset to account for the absence of flow data provided by company 12

ID	Sector	Company type	Data source	Weather station
1	1	Biopharmaceuticals	AER	2
2		Biopharmaceuticals	AER	5
3		Small molecule pharmaceuticals	AER	2
4		Biopharmaceuticals	AER	4
5		Small molecule pharmaceuticals	AER	2
6	2	Food	AER	8
7		Beverage	AER	5
8		Food	Company	3
9		Beverage	Company	5
10		Food/beverage	Company	3
11	3	Waste management	AER	4
12		Waste management	Not available	7
13		Landfill	AER	1
14		Landfill	AER	6
15		Landfill	AER	1
16*		Waste management	AER	2

Data analysis was performed using the R software package (version 3.6.2) and the RStudio Integrated Development Environment (version 1.2.5033). Data visualisation was performed using the ggplot2 package, linear modelling was performed using the modelr and broom packages, principle component analysis was performed using factoextra and FactoMineR, correlation analysis was visualised with the corrplot and ggpairs packages.

Results and discussion

Annual TE outputs

TE volume and flow data was evaluated over the 2015 to the 2019 period and summary data on average annual TE volumes in cubic meters (m^3), average daily flow rate in cubic meters per day (m^3/d), flow rate standard deviation, median daily flow rate, and number of observations (n) is tabulated in Table 23.

Table 23 Summary of industry TE flow data for the 2015 to 2019 period. Note that n = number of observations

Sector	Year	Average annual TE volume (m³)	Average daily flow (m³/d)	Standard deviation daily flow (m³/d)	Median daily flow (m³/d)	n
Biopharmachem (1)	2015	95271.8	261	78.8	411.9	4
	2016	113042.6	309.7	103.2	478.1	4
	2017	107704.6	295.1	86.5	468.5	4
	2018	118004.6	323.3	128.3	470	4
	2019	72461	291.3	120.9	392.6	3
Food/beverage (2)	2015	130300.7	357	357	NA	1
	2016	185525.2	508.3	508.3	162.1	2
	2017	121861.6	333.9	292.5	261.1	4
	2018	108891.7	306.3	173.4	250.5	5
	2019	112659.3	320.6	185	257.8	3
Waste management (3)	2015	8882.1	22.4	21.2	15.7	5
	2016	10812.3	27.7	15.8	21.9	6
	2017	10703.6	27.6	17.8	21	6
	2018	8849.6	22.8	19.6	17.7	6
	2019	7014.9	18.6	17.1	17.9	6

The following figures summarise the annual variation in average daily TE emissions for the three sectors assessed. The present data indicate that the year-to-year TE emissions for the three sectors is relatively stable and not increasing over time.
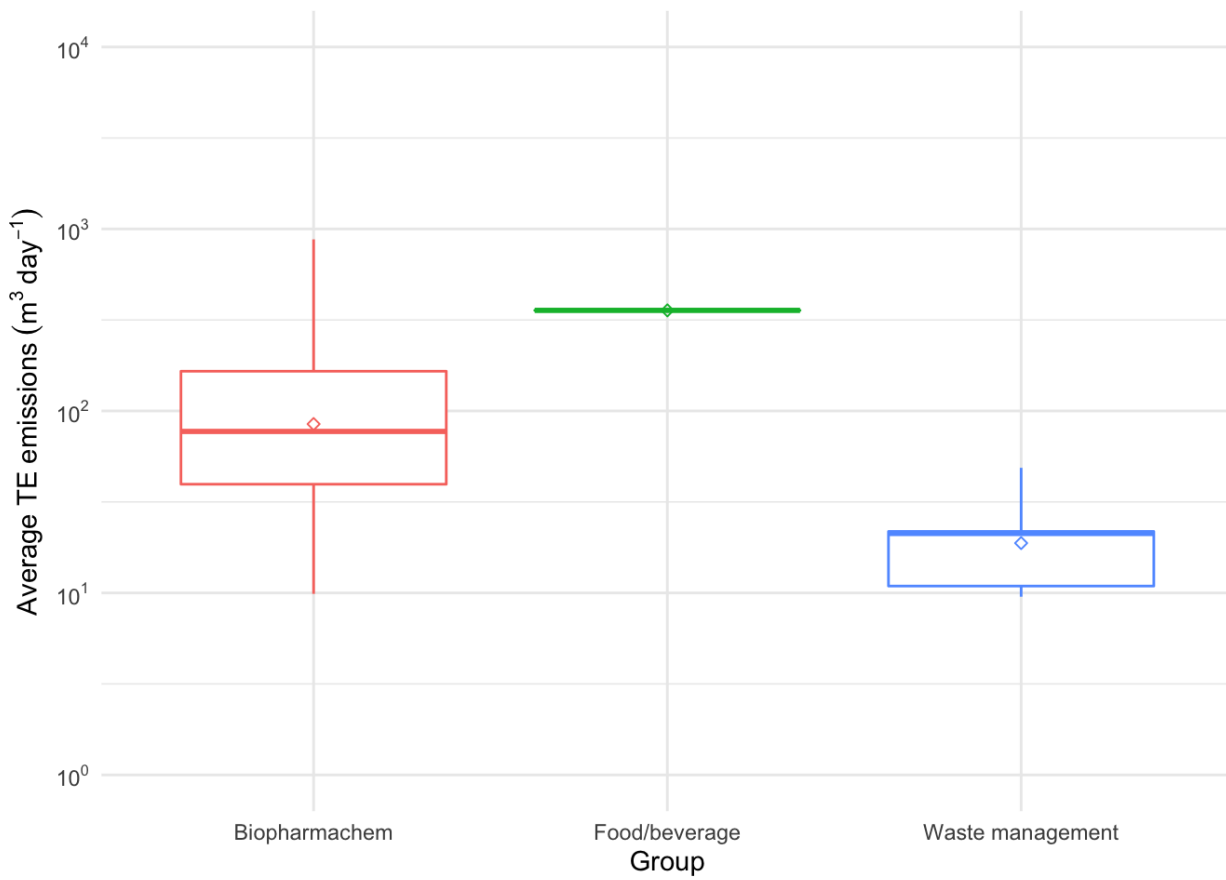
Figure 28 Average daily flow rate of TE groups for 2015. The box plots shows the distribution of emissions, median value (cross bar), average value (diamond) along with the interquartile range (whiskers)
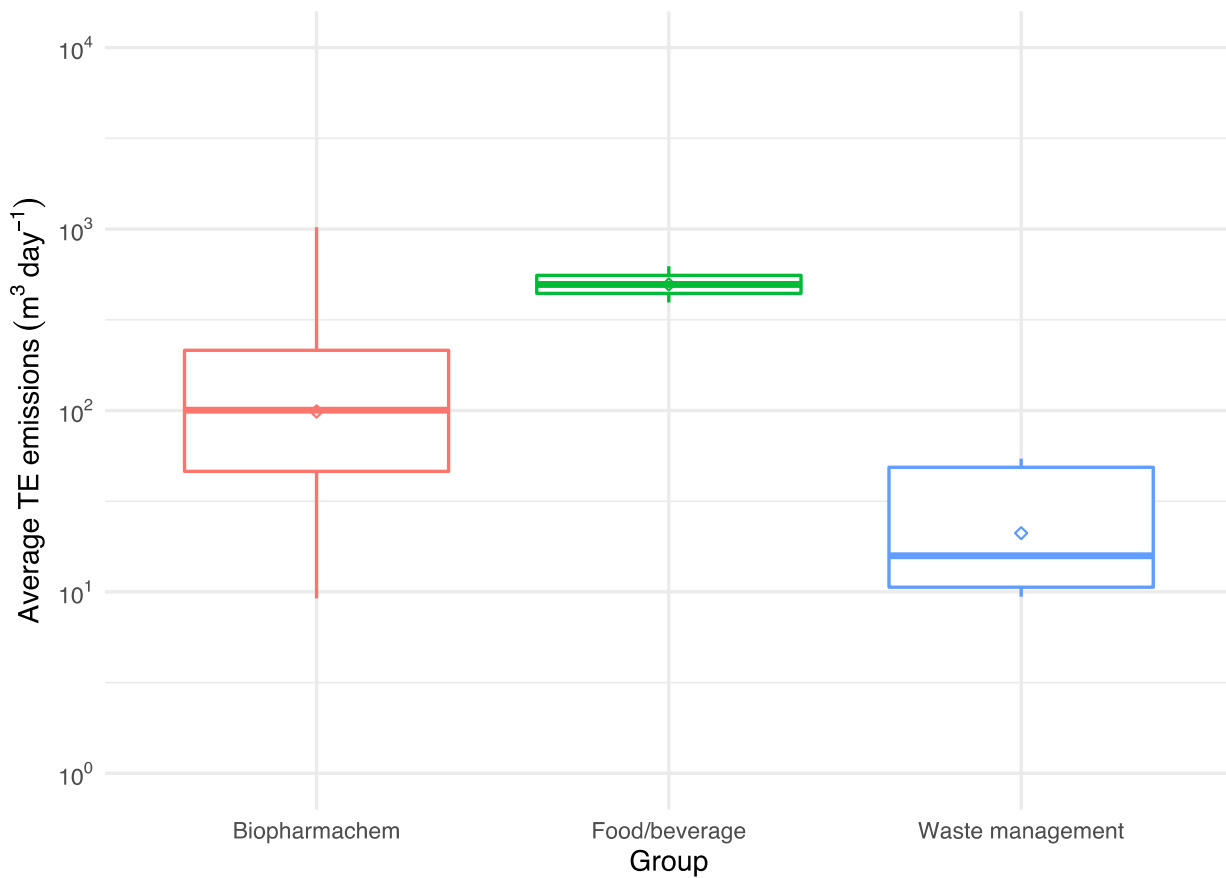
Figure 29 Average daily flow rate of TE groups for 2016. The box plots shows the distribution of emissions, median value (cross bar), average value (diamond) along with the interquartile range (whiskers)
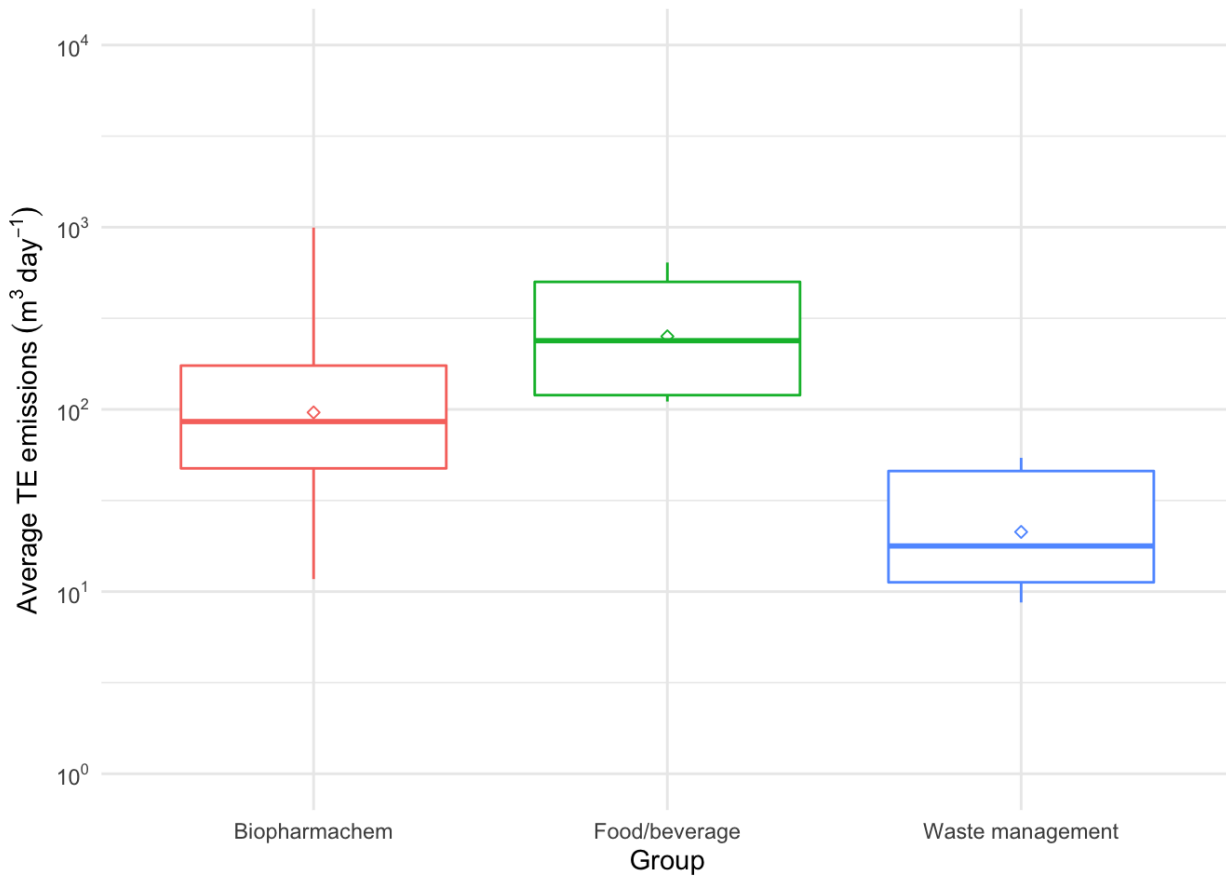
Figure 30 Average daily flow rate of TE groups for 2017. The box plots shows the distribution of emissions, median value (cross bar), average value (diamond) along with the interquartile range (whiskers)
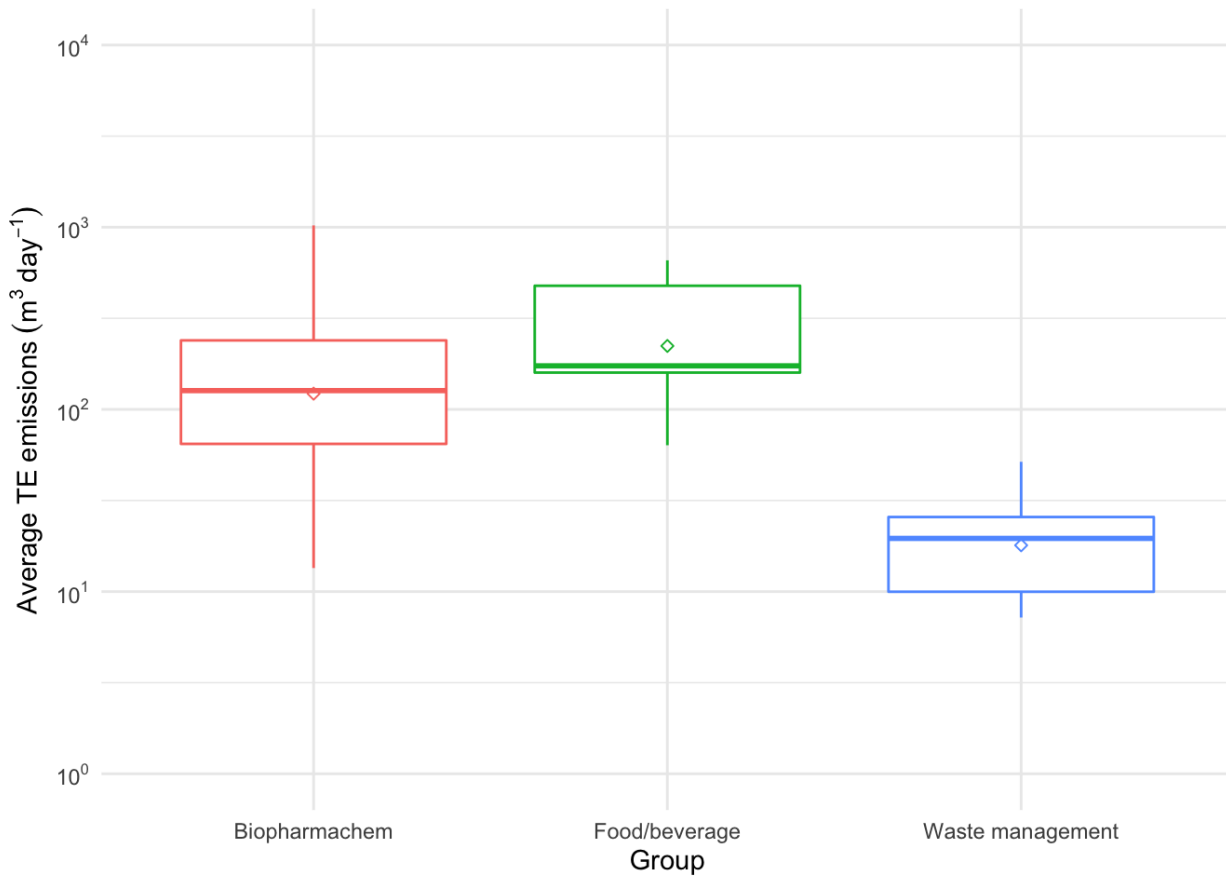
Figure 31 Average daily flow rate of TE groups for 2018. The box plots shows the distribution of emissions, median value (cross bar), average value (diamond) along with the interquartile range (whiskers)
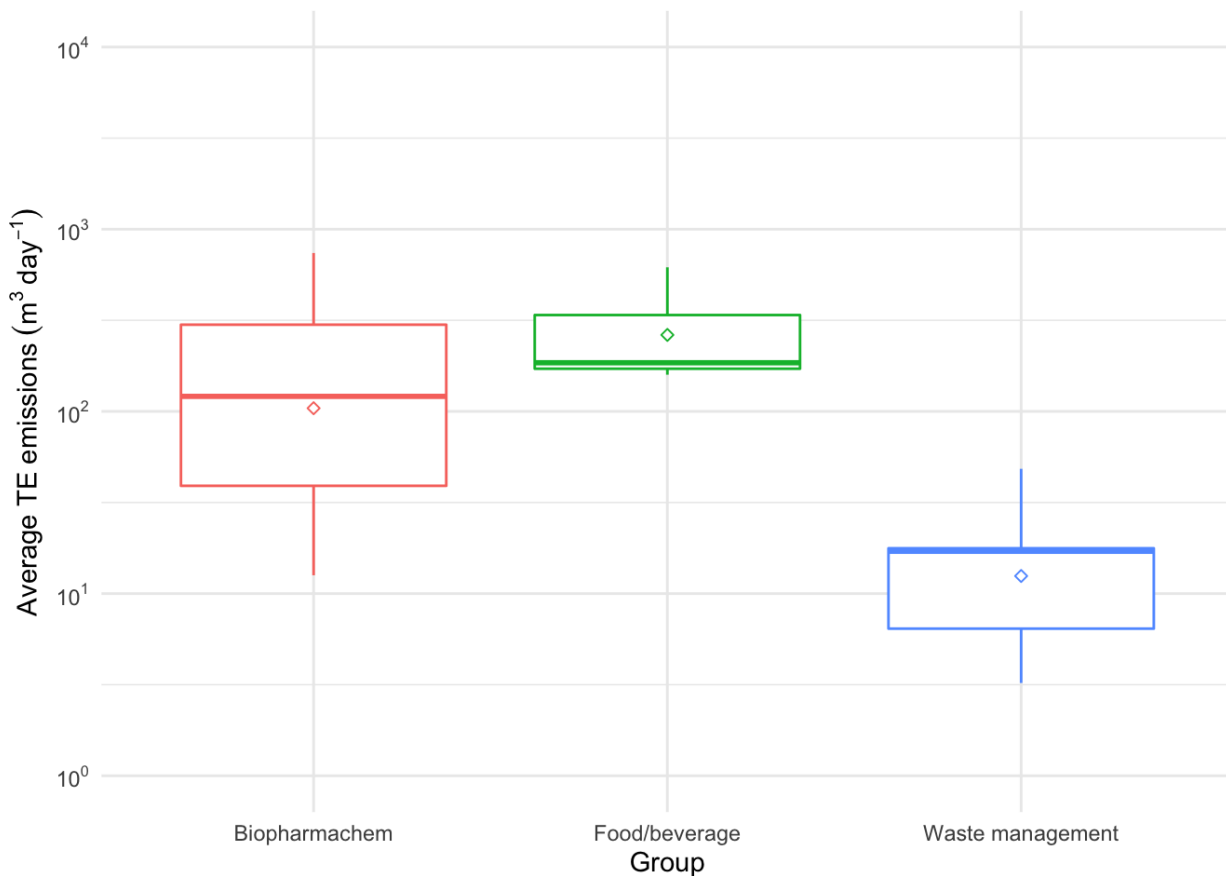
Figure 32 Average daily flow rate of TE groups for 2019. The box plots shows the distribution of emissions, median value (cross bar), average value (diamond) along with the interquartile range (whiskers)

When the annual flow volumes for the 2015 to 2019 period are averaged, the food/beverage sector was found to emit significantly larger (Figure 33) daily volumes of TE compared to the biopharmachem (p = 3.1e-2, α = 0.05) or waste management sectors (p = 4.1e-10, α = 0.05). While the biopharmachem also produced significantly more TE than the waste management sector (p= 7e-04, α = 0.05). Both the biopharmachem and food/beverage sectors emitted a wide range of TE volumes, and some biopharmaceutical sites produce greater amounts of TE than the food/beverage sector. In general the volumes of TE, produced by industry followed the rule of; food/beverage > biopharmachem >> waste management. The differences between the scale of production and hygiene requirements for the food/beverage and biopharmachem sectors are the most likely reasons for the differences between water consumption between these sectors, however this is outside the scope of the present report.
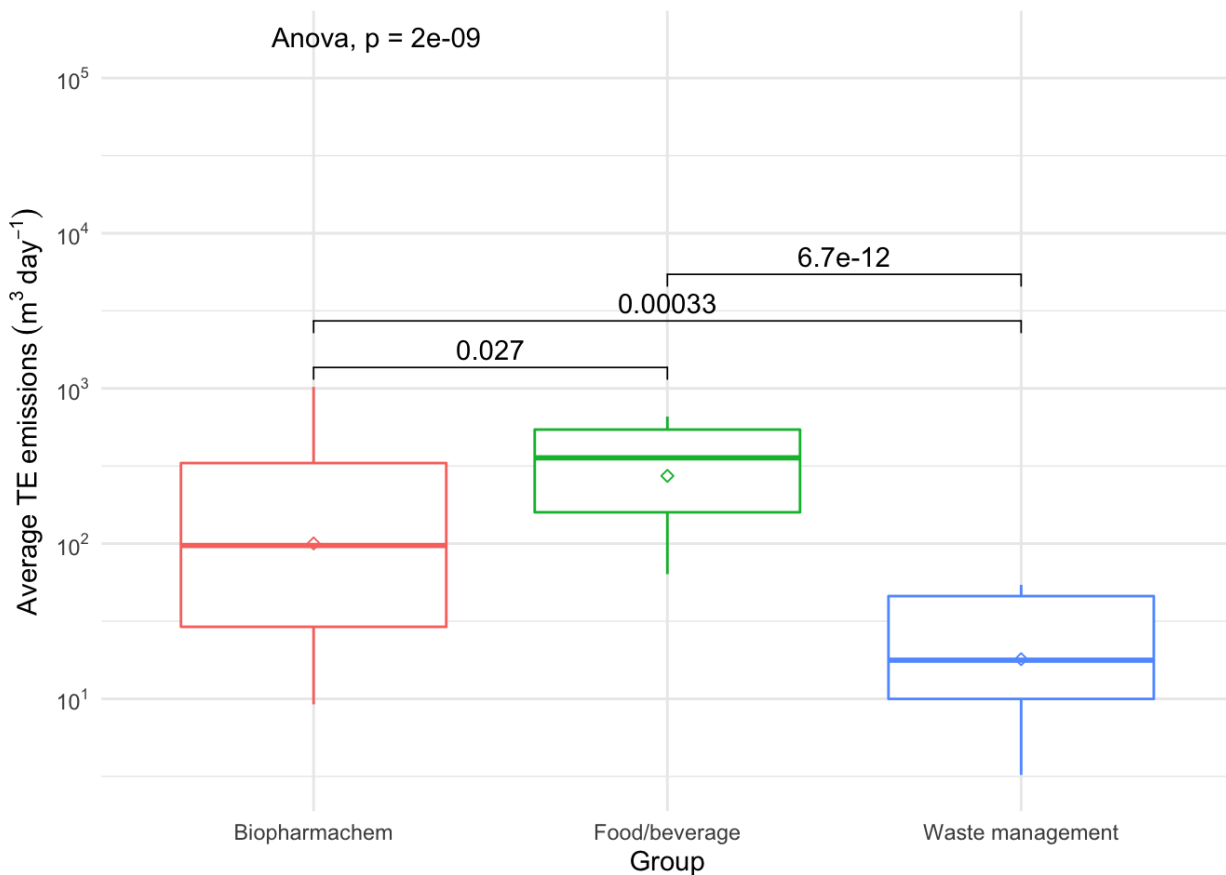
Figure 33 Average TE emissions per day for each industrial sector. Statistical testing using ANOVA (95% confidence level)

The waste management sector produced 1 to 2 order of magnitude less TE than the other two sectors, indicating a substantial difference in the usage of water at waste management sites. The amount of TE in the form of leachate produced by landfill sites is affected by the stage of the lifecycle relevant to the given landfill. Landfills that are in the process of being filled may have higher volumes of TE generated until they are capped with a butyl liner, however none of the sites presently included were being actively filled. Landfills also generate lower volumes of leachate as they age as contents degrade. The lower level of TE production in the waste management sector compared to the biopharmaceutical and food/beverage sectors is likely linked to the use of water as a solvent/material in production and the stringent cleaning requirements for products produced by these two sectors. The variability in the TE emissions from each sector is also determined by the scale of each company's operations, the types of operations being undertaken and the emission limits imposed by their respective TE licenses, however the typical averages can be used to inform the impact that new facilities may have on sewer inputs.

Evaluation of the impact of rainfall on TE dilution

Rainfall levels at each site was assessed by obtaining rainfall data from weather stations maintained by Met Éireann ("Historical Data - Met Éireann - The Irish Meteorological Service," 2020). Weather stations were selected based on proximity of each station to an industrial site (less than 15 km) along with the availability of daily rainfall measurements covering the requisite 2015 to 2020 period. Table 22 indicates which weather stations correspond to each project site. A selection of 8 weather stations was able to provide rainfall data linked to the industrial sites in this study and daily rainfall levels for the 2015 to 2019 period is shown in Figure 34.
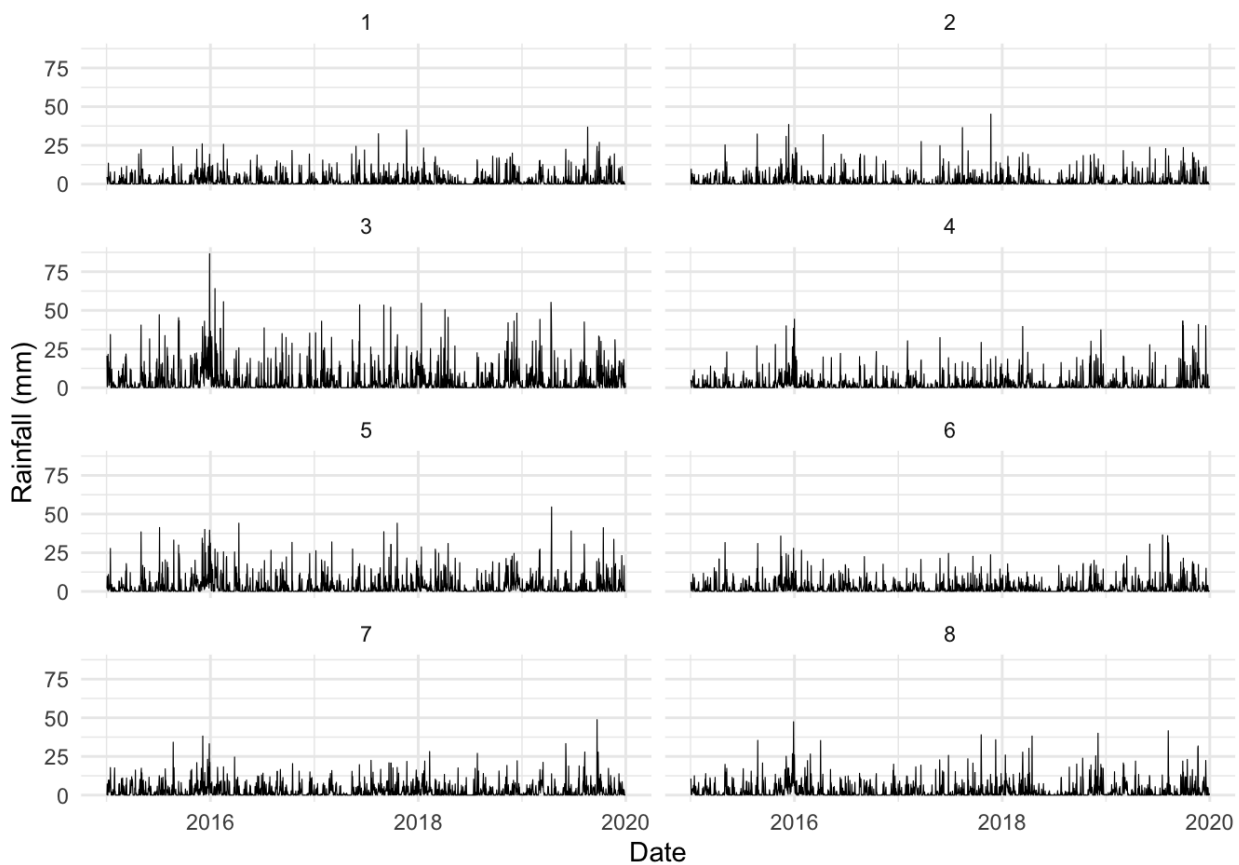
Figure 34 Daily rainfall for each weather station (1 to 8) associated with the TE projects industrial sites

Daily rainfall amounts were summarised to provide annual rainfall levels (Figure 35) to allow for a comparison with company reported annual TE emissions.
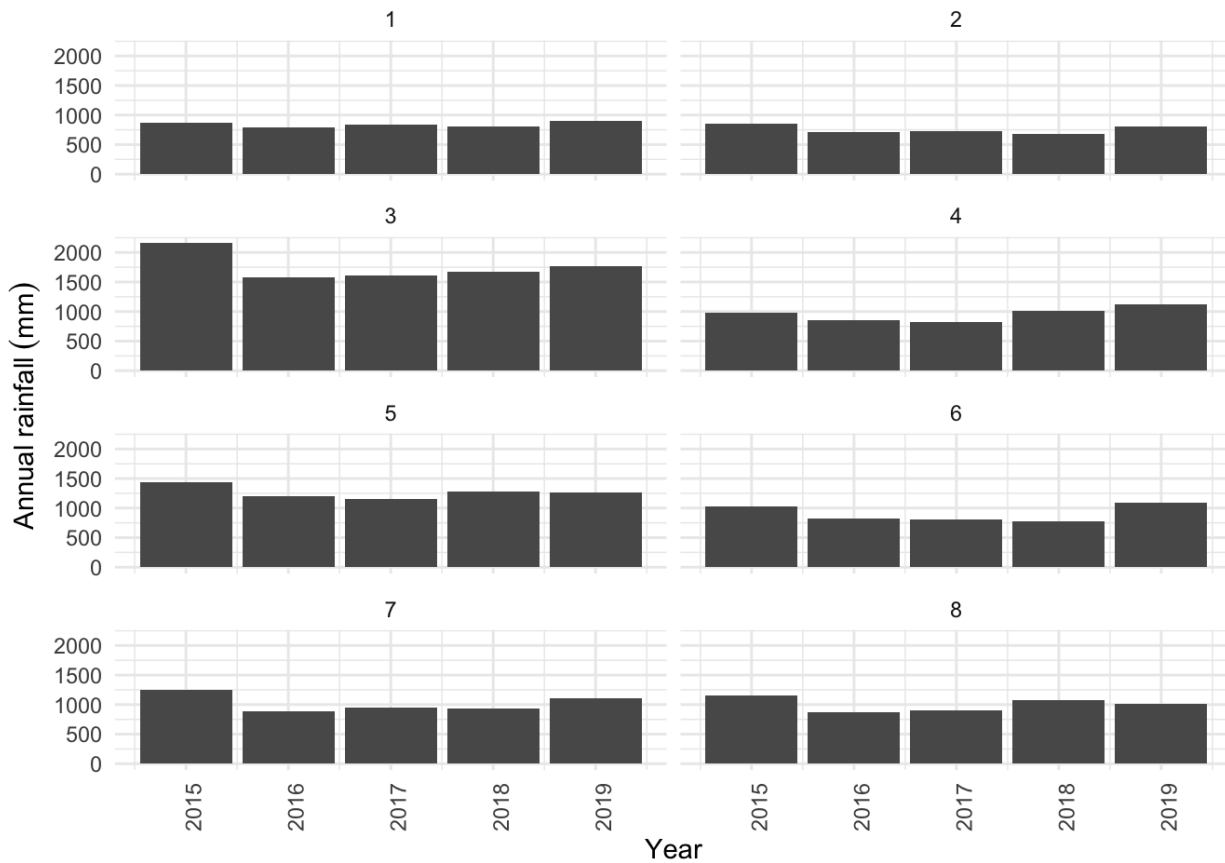
Figure 35 Annual rainfall levels (mm) for each of the 8 weather stations used for evaluating the impact of rainfall on industry sites

Table 24 summarises the average rainfall amounts and additional information about the variation of rainfall across the 8 rainfall groups relevant to the company sites included in this study. The average variation in rainfall for each site was between 5.8 and 16.0 % and the amounts of rainfall varied across the range of 685 mm to 2156 mm over the 2015 to 2019 period.

Table 24 Summary table of the average rainfall, standard deviation (SD) of rainfall, rainfall variation (%) and the minimum and maximum rainfall levels observed at each weather station

Weather station	Average rainfall (mm)	SD rainfall (mm)	Rainfall variation (%)	Maximum Annual rainfall (mm)	Minimum Annual rainfall (mm)
1	840.1	48.8	5.8	907.2	785.5
2	755.3	70.0	9.3	848.7	685.1
3	1758.0	235.0	13.4	2156.1	1574.0
4	952.2	121.1	12.7	1114.5	819.2
5	1267.5	103.4	8.2	1432.3	1161.4
6	904.3	144.4	16.0	1093.1	772.6
7	1027.2	151.2	14.7	1249.1	883.6
8	1001.4	114.7	11.5	1150.8	877.7

The impacts of rainfall on TE emissions was evaluated by comparing annual rainfall levels with annual TE emissions data for each site. The impact of rainfall on the generation of TE is dependent on how exposed a sites TE system is to contributions from rainfall. Some companies have open TE systems that allow the capture of rainfall in addition to the TE generated during site operations, while others use closed systems. An example of rainfall contributing to TE volumes is due to rainfall on bunded areas that divert rainfall to TE rather than allowing runoff to the environment or storm water drains or other dedicated interceptors. Rainfall captured in TE systems thus increases TE volumes, while also effecting the levels of compounds and particulates present. Biopharmachem, food/beverage and waste management companies may operate TE balancing tanks or treatment reactors that are open to the atmosphere depending on their design. These open vessels are susceptible to rainfall, which can dilute the composition of TE, while increasing the volume of TE that is later emitted to sewer. The contribution of rainfall to TE volumes to such systems is anticipated to be quite low since companies usually construct their TE systems to minimise the amount of TE generated, by enclosing their systems or implementing rainwater diverters to minimise the impact rainfall has on TE volumes. Landfill sites are similarly typically encapsulated by butyl liner cells that prevent the release of leachate to the environment and accumulation of rainfall in landfill cells. Landfills that are in the process of being filled are susceptible to rainfall increasing the volume of TE generated however the present study did not include such sites. Usually rainfall is diverted from landfill to prevent the generation of excessive volumes of TE, using bunded boundaries, interceptors and drainage to stormwater or local streams.

Table 25 provides a numerical summary of the annual flow data for the three sectors over the 2015 to 2019 period. The biopharmachem and food/beverage sectors emitted TE volumes one order of magnitude greater than the waste management sector on average. Median values of TE flows indicated a narrower difference between sectors, although the levels emitted by the waste management sector were still lower than the other two sectors. The biopharmachem sector had the largest variation in TE emissions outputs.

Table 25 Summary of annual TE volumes (m³) emitted per year. Averages of the annual TE emissions for the 2015-2019 period

Group	Median	Average	SD	Maximum	Minimum
Biopharmachem	40621	121049	146525	357580	4153
Food/beverage	55420	101113	89455	231669	15665
Waste management	10668	10668	4889	17753	5563

Daily emissions of TE are summarised in Figure 36 and Table 26 below. The trends in daily TE emissions outputs matched those of the annual emissions.
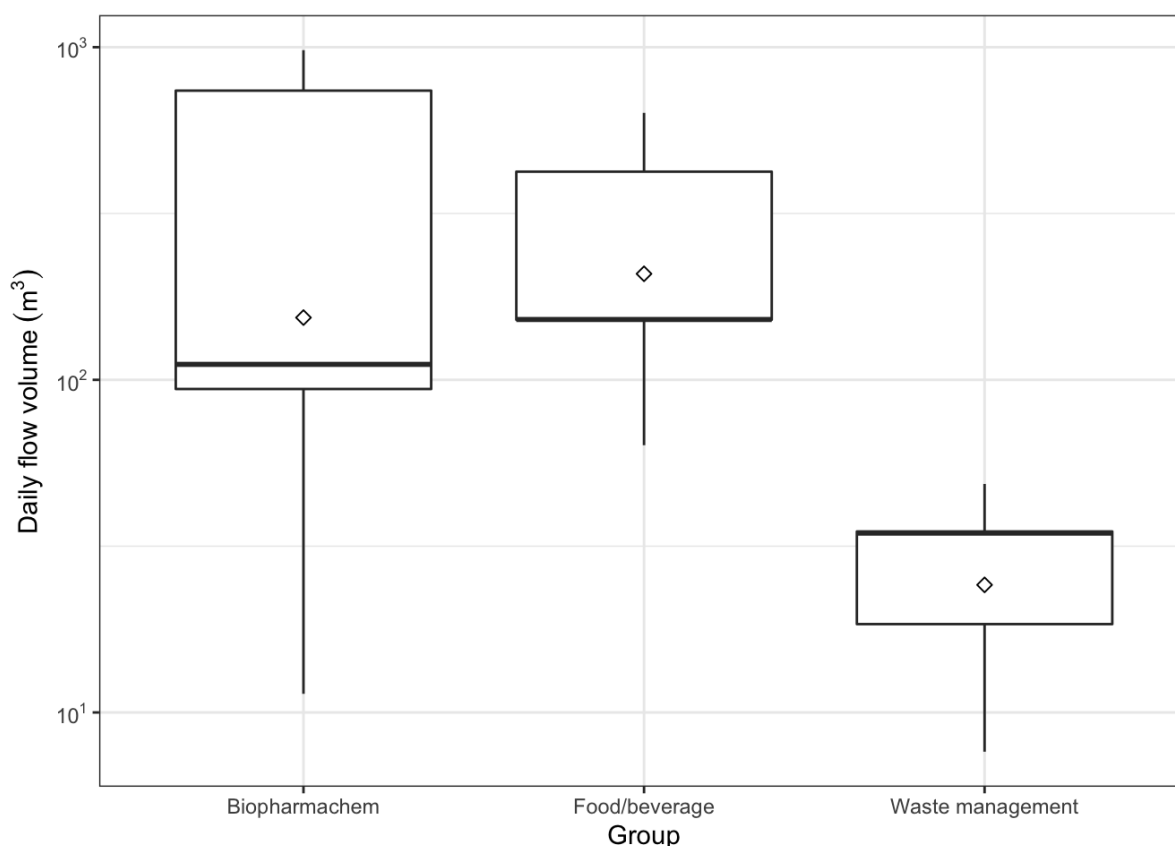
Figure 36 Averaged daily flow volume (m³) summary for TE outputs from three industrial groups

The ranges of TE emissions were highest and most variable within the biopharmachem sector, likely due to the stringent requirements of cleaning required during production, similarly the food/beverage sector also featured higher water compared to the waste management sector.

Table 26 Summary of TE flow volumes (m^3 d^{-1}) emitted per day. Averages of the daily TE emissions for the 2015-2019 period

Group	Median	Average	SD	Maximum	Minimum
Biopharmachem	111.3	387.3	441.3	979.7	11.4
Food/beverage	151.8	284.8	237.6	634.7	63.6
Waste management	34.6	28.9	16.0	48.6	7.6

The impact of rainfall on the volume of TE generated by each company was assessed using linear regression modelling. Sites 1, 10 and 12 were excluded from modelling, as sites 1 and 10 only provided 1 year of flow data, and annual flow was unavailable for site 12.

The regression models for the biopharmachem companies are shown in Figure 37. No significant linear relations were found for this sector, despite company 2 and 4 having open TE systems in the form of balancing tanks and TE treatment reactors. The wide confidence intervals of the plots suggest that TE volume was uncorrelated with annual rainfall events. The relatively small surface area of the open balancing tank vessels minimised the impact of rainfall events on annual TE volumes produced by these companies.
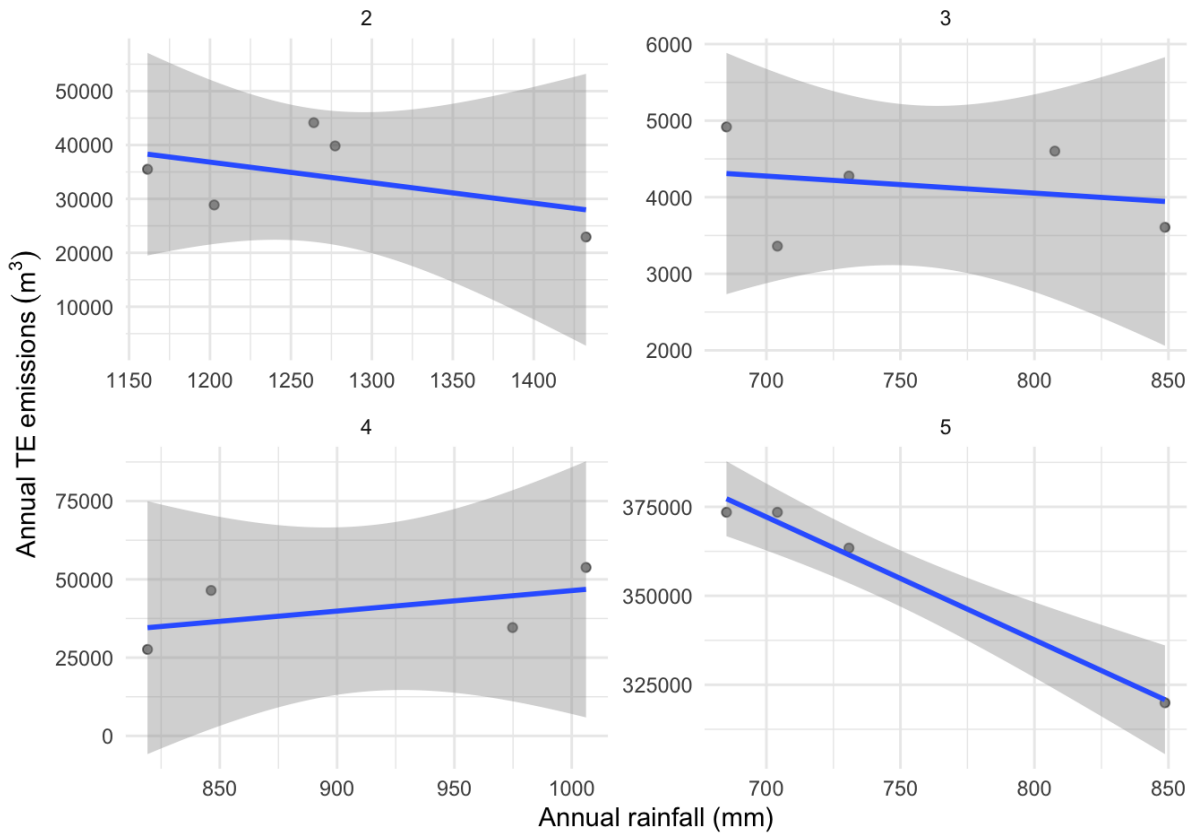
Figure 37 Evaluation of the impact of rainfall on annual TE emissions for the biopharmaceutical sector including project companies 2, 3, 4, 5 and the additional company 16. The blue line shows the best fit line provided by linear regression and grey region shows the confidence interval of the linear regression model

The linear regression fits of the food/beverage sector are shown in Figure 38, and all sites showed no significant correlations between rainfall levels and annual TE volumes. Sites 6 and 8 had open TE systems with exposed reactors or balancing tanks that could accumulate low levels of rainfall. However, this rainfall exposure did not lead to the generation of significantly larger volumes of TE annually
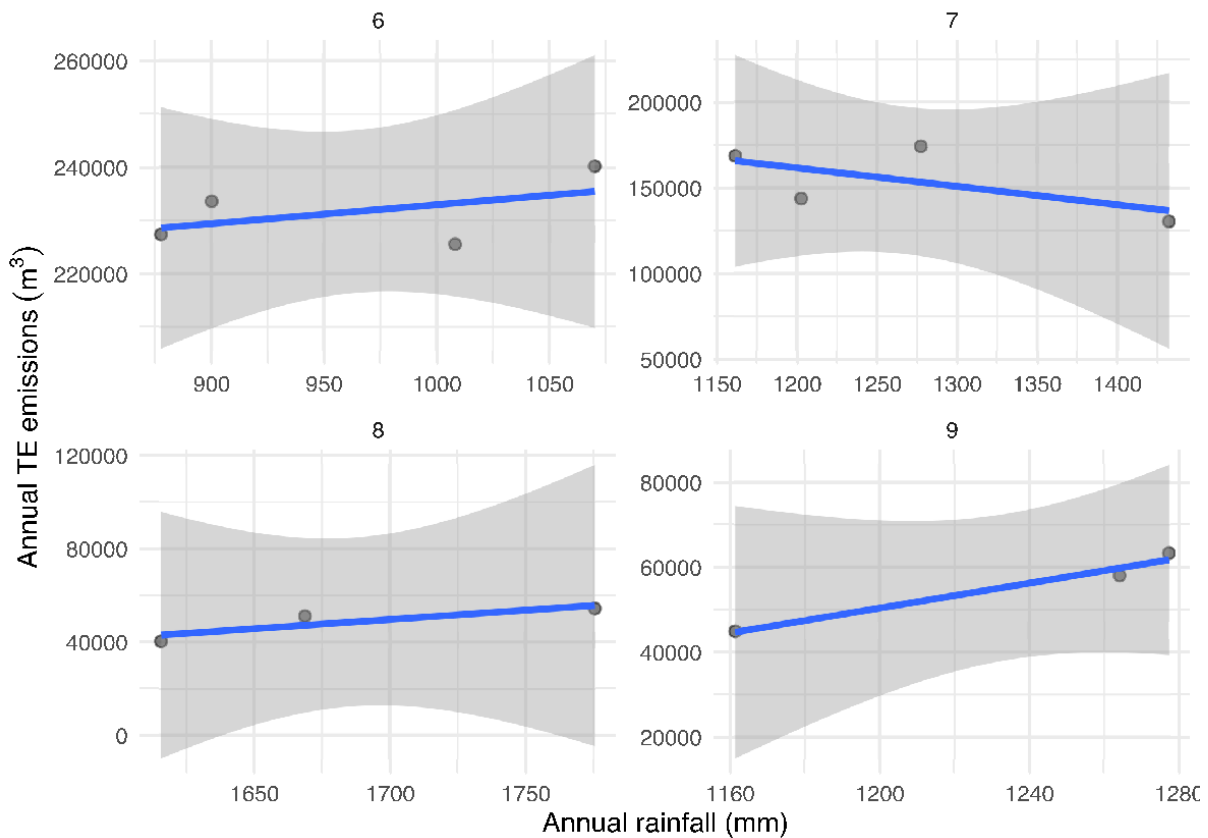
Figure 38 Evaluation of the impact of rainfall on annual TE emissions for the food/beverage sector including project companies 6, 7, 8, 9, and additional companies 17, 18, 20, 26, 27. The blue line shows the best fit line provided by linear regression and grey region shows the confidence interval of the linear regression model

Finally, linear regression models between annual rainfall and TE volume for the waste management sector are presented in Figure 39. The waste management and landfill sites studied again did not provide evidence for a correlation between the annual volume of TE generated and rainfall levels.
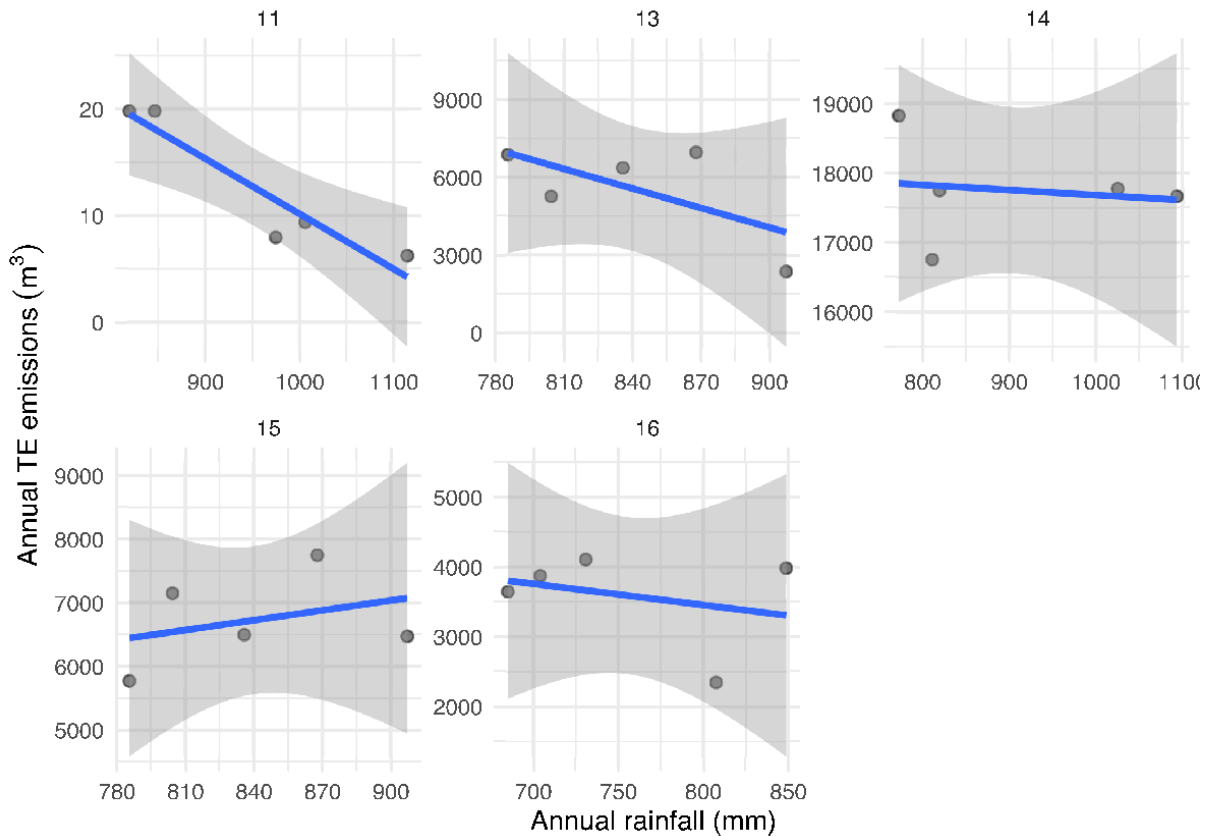
Figure 39 Evaluation of the impact of rainfall on annual TE emissions for the waste management sector including project company 11, and additional companies 21, 22, 23, 24, 25. The blue line shows the best fit line provided by linear regression and grey region shows the confidence interval of the linear regression model

To confirm that there was no sector wide link between annual flow and rainfall, the annual TE emissions and rainfall levels for each company, site and year were normalised using mean-centring. This normalisation allows for direct comparison of the variances of annual rainfall and TE volume between different sites of each sector as shown in Figure 40.
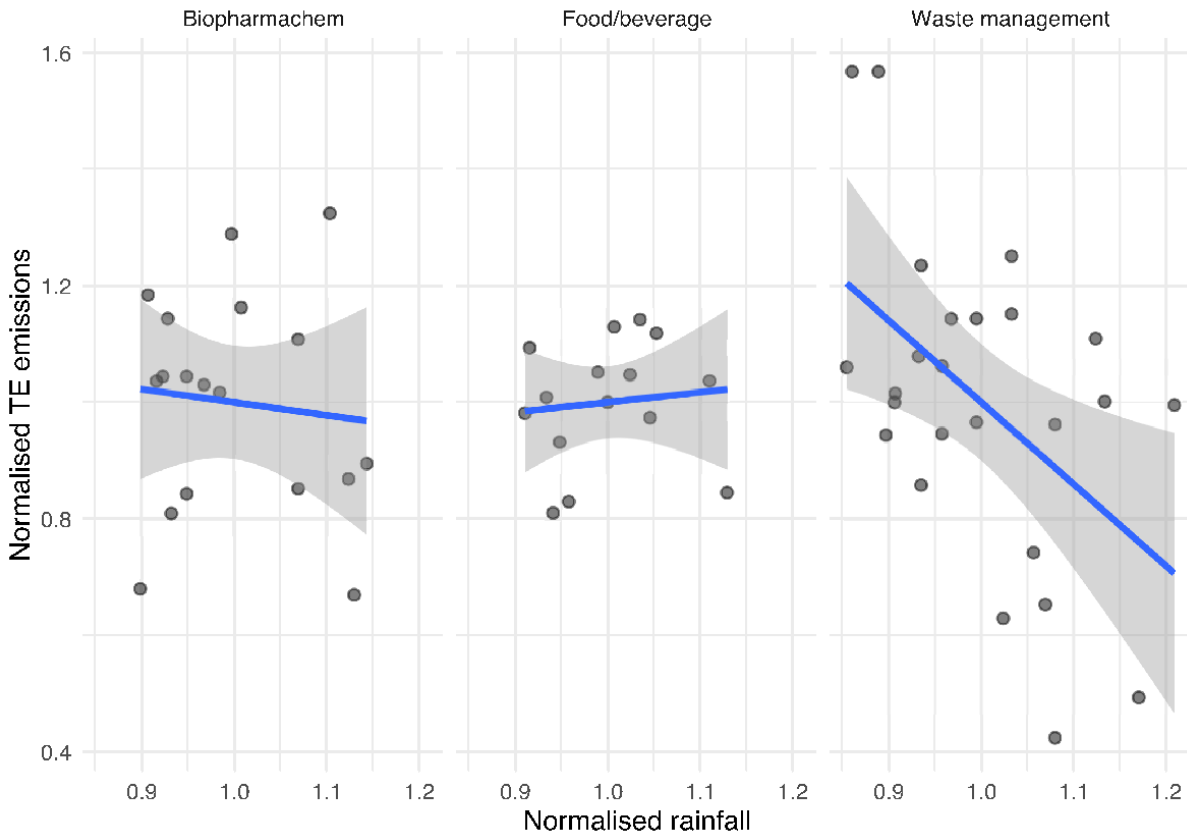
Figure 40 Normalised rainfall vs normalised TE emissions for the biopharmachem, food/beverage and waste management sectors. The blue line shows the best fit line provided by linear regression and grey region shows the confidence interval of the linear regression model

The normalised data for the three sectors indicated that there was insufficient evidence for a linear relation between TE volume and rainfall at the sector level despite controlling for the different levels of TE volume outputs and the different rainfall levels associated with each site.

Opportunities for the recovery of organic and inorganic species from TE

Calculation of annual mass loadings of organic and inorganic species was performed using the flow data and measurements performed on TE samples obtained from each company. Figure 41 shows the variation of ammonia, chloride, COD, nitrate, nitrite, phosphate, sulphate, TN, TOC and TP outputted annually by each of the three sectors.
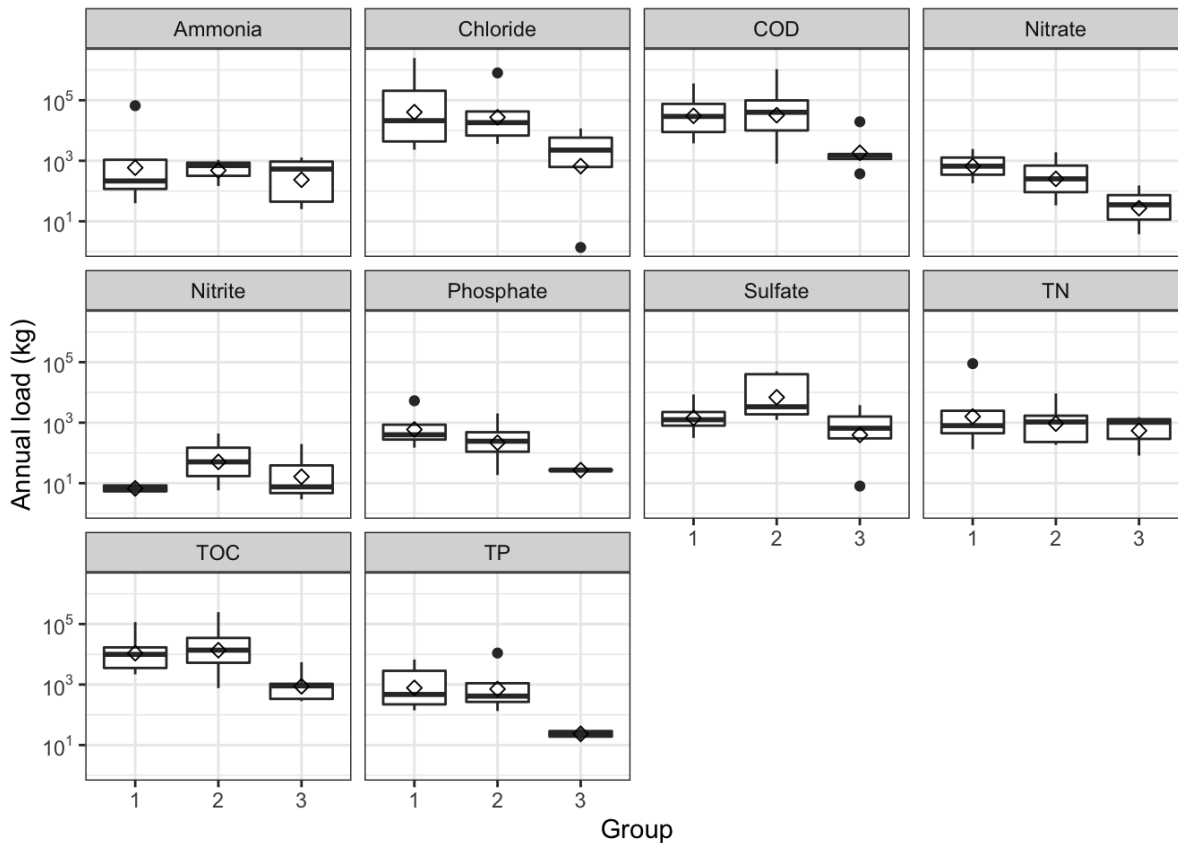
Figure 41 Annual loads of selected nutrient species monitored in each of the three industrial groups (1 = biopharmachem, 2 = food/beverage, 3 = waste management)

Table 27 summarises the TE parameter outputs measured for the biopharmachem sector. The median annual outputs of ammonia, nitrate, nitrite, phosphate, TN, and TP were less than 1000 kg for this group, while median outputs of COD, chloride and TOC were above this threshold. The largest outputs were COD and chloride with median outputs of 21,000 and 29,000 kg respectively. Some biopharmachem companies were outputting larger quantities of ammonia, nitrate, phosphate and TP compared to the median, which manifests as inflated average outputs for these parameters. Median outputs of ammonia were on the order of 169 kg, while the average outputs were 13,000 kg which suggests that some biopharmachem sites may benefit more from nitrogen recovery technologies than others. Opportunities for recovering phosphorous were on the order of 1000 to 2000 kg annually per site.

Table 27 Summary of annual emissions (kg) of nutrient parameters for the biopharmachem group

Group	Measurement	Median	Average	SD	Max	Min
1	Ammonia	169	13327	29530	66152	0
1	Chloride	21142	543940	1088896	2485797	2321
1	COD	29230	95427	150260	359368	3768
1	Nitrate	90	658	1198	2450	0
1	Nitrite	0	3	5	11	0
1	Phosphate	339	1249	2266	5290	0
1	Sulphate	1089	2281	3560	8565	0
1	TN	799	18649	39558	89395	132
1	TOC	9949	29761	48682	116213	2180
1	TP	472	2082	2828	6729	141

The outputs of the food/beverage sector indicated median outputs of chloride, COD, sulphate, TOC over the range of 13,000 to 40,000 kg, with average outputs between 174,000 and 242,000 kg. Average outputs of ammonia where 384 kg, with a maximum output of 1000 kg, which was lower than the ammonia levels detected in biopharmachem TE. The levels of TN were somewhat higher than ammonia with outputs on average of 2500 kg per annum. Phosphate outputs were on the order of 634 kg per annum, with a maximum output of 2000 kg. TP amounts (2400 kg average) were somewhat higher than phosphate, indicating that phosphorous was primarily bound in organic molecules rather free in solution as orthophosphate.

Table 28 Summary of annual emissions (kg) of nutrient parameters for the food and beverage group

Measurement	Median	Average	SD	Max	Min
Ammonia	146	384	483	1079	0
Chloride	18226	174578	350904	801697	3596
COD	40040	242606	460334	1063216	804
Nitrate	17	484	946	1902	0
Nitrite	0	89	196	439	0
Phosphate	249	634	930	2018	19
Sulphate	3350	19228	23643	49741	1237
TN	1053	2489	3847	9278	185
TOC	13726	60452	105514	247750	762
TP	336	2398	4817	11007	0

Annual TE outputs of nutrient and wet chemistry parameters were lower in the waste management sector (Table 29), primarily due to the order of magnitude lower volumes of TE generated by this sector (Table 25). Outputs of COD, chloride, TOC, TN and sulphates were between 1000 and

5000 kg per annum. The levels of nitrates, nitrite, phosphate and TP were all below 100 kg per annum.

Table 29 Summary of annual emissions (kg) of nutrient parameters for the waste management group

Measurement	Median	Average	SD	Max	Min
Ammonia	533	564	551	1278	25
Chloride	2258	4076	4816	11689	1
COD	1516	4834	8206	19487	371
Nitrate	19	48	72	153	0
Nitrite	5	52	97	198	0
Phosphate	13	14	16	29	0
Sulphate	655	1273	1536	3804	8
TN	1031	846	632	1525	82
TOC	905	1613	2188	5480	284
TP	0	10	16	36	0

The daily loads for nutrients outputted by the three sectors was also calculated and summarised in Figure 42 to provide insight into the daily contributions of these species to sewer networks.

Figure 42 Daily loads of selected nutrient species monitored in each of the three industrial groups (1 = biopharmachem, 2 = food/beverage, 3 = waste management)

Opportunities for the recovery of metals and inorganic species from TE

Levels of metals and additional inorganic parameters were measured in TE samples from each of the companies included in the study using ICP-OES. The most frequently detected species in TE were aluminium, calcium, iron, potassium, magnesium, manganese, sodium, phosphorous and sulphur. These measurements were combined with flow data to provide estimates of annual contributions of these species to sewer networks. Additional metals that were measured but not detected at appreciable levels were silver, arsenic, barium, beryllium, bismuth, cadmium, cobalt, copper, chromium, gallium, indium, lithium, nickel, lead, rubidium, selenium, strontium, tellurium, vanadium and zinc. These metals were excluded from further mass loading calculations.

Figure 43 Annual loads of selected metals monitored in each of the three industrial groups (1 = biopharmachem, 2 = food/beverage, 3 = waste management)

Table 30 summarises the TE loadings for the biopharmachem sector. Sodium was the most prevalent metal detected in biopharmachem TE with median annual outputs of 16,000 kg to sewer. Potassium was next most prevalent metal emitted with an average annual output of 2600 kg and a median output of 4500 kg. Potassium is a potentially interesting target for recovery due to its usage in fertiliser products. Levels of aluminium, iron, magnesium and manganese were all low with outputs of less than 100 kg.

Table 30 Summary of annual emissions (kg) of metals/inorganics measured in TE derived from the biopharmachem group

Measurement	Median	Average	SD	Max	Min
Al	4	4	4	7	2
Ca	1003	4220	7008	16725	613
Fe	24	25	11	35	15
K	2629	4563	5951	12855	140
Mg	152	307	395	1010	75
Mn	1	1	NA	1	1
Na	16661	385016	771409	1761318	4659
P	611	925	1021	2592	88
S	828	1656	2124	4805	165

Table 31 summarises the outputs of metals from the food/beverage group. Similar to the biopharmachem sector, sodium was the largest species emitted in TE (median output of 17,000 kg). Elevated levels of aluminium were detected (median 159 kg, average 429 kg) in food/beverage TE due to the use of dissolved air flotation processes used at some of the TE sites that requires the addition of aluminium containing flocculants. Approximately 9000 kg of potassium was emitted from each of the food/beverage sites annually. Sulphur levels were approximately 10,000 kg per annum, compared to the 1600 kg released by the biopharmachem group. Both potassium and sulphate are potentially of interest for recovery purposes as these species are components of fertilisers used in agriculture (Solon et al., 2019).

Table 31 Summary of annual emissions (kg) of metals/inorganics measured in TE derived from the food/beverage group

Measurement	Median	Average	SD	Max	Min
Al	159	429	445	1004	23
Ca	3835	7979	10738	23854	391
Fe	42	68	72	150	13
K	8014	8936	6450	17218	2498
Mg	175	1482	2697	5526	51
Mn	97	97	NA	97	97
Na	33023	105679	164404	396807	5249
P	268	874	1316	2840	122
S	6916	10148	11037	25349	1410

The annual TE outputs of the waste management sector are summarised in Table 32 below. The annual amounts outputted by this sector were lower than those calculated for the biopharmachem and food/beverage sectors due to the lower amounts of flow emitted by this sector as highlighted

in Table 25 and Figure 36. The most significant species outputted by the waste management sector were calcium and sodium while the other annual outputs were all below 1000 kg per annum.

Table 32 Summary of annual emissions (kg) of metals/inorganics measured in TE derived from the waste management group

Measurement	Median	Average	SD	Max	Min
Al	26	78	121	257	2
Ca	1240	1351	944	2607	318
Fe	54	50	44	89	4
K	671	604	440	1065	10
Mg	239	239	NA	239	239
Mn	7	6	3	8	1
Na	1147	1698	1535	4328	402
P	10	10	3	14	7
S	625	814	663	1551	267

The daily inputs of these species was calculated based on averaged daily flow data (Table 26), and summarised in Figure 44.
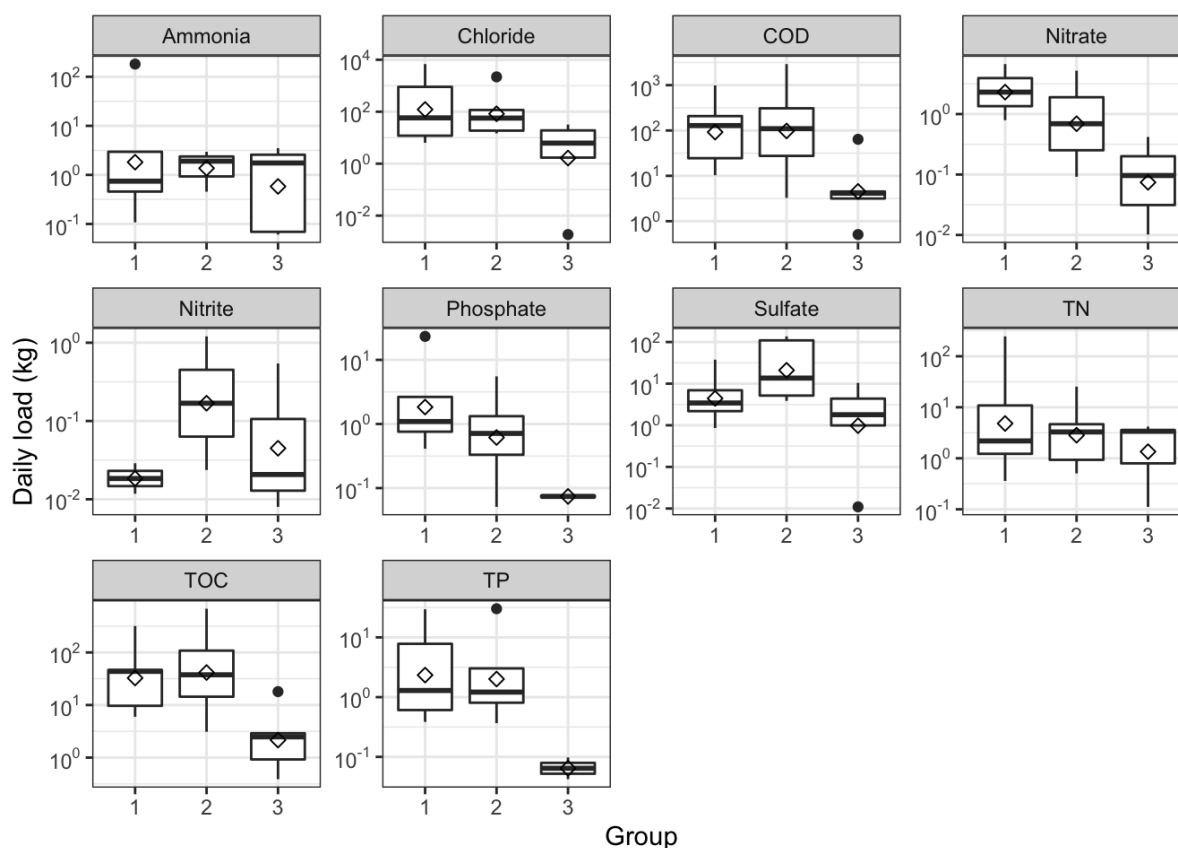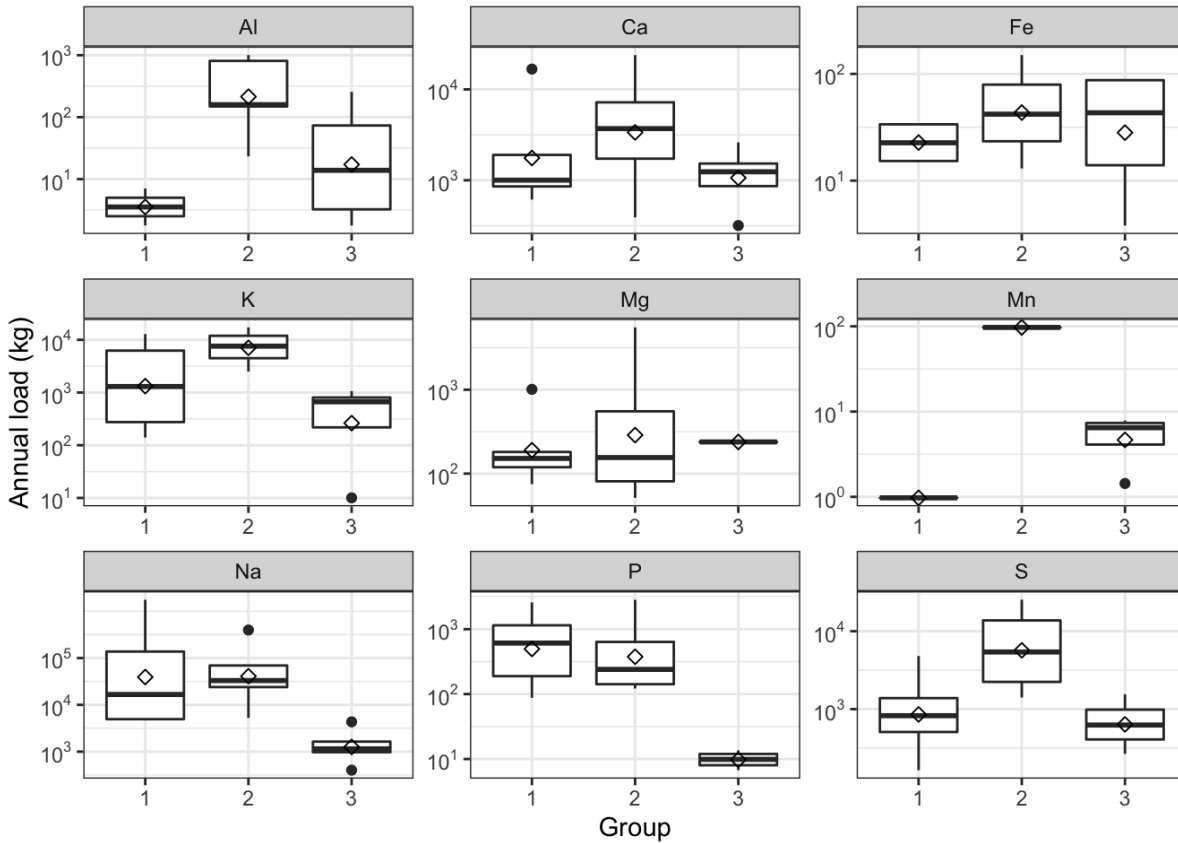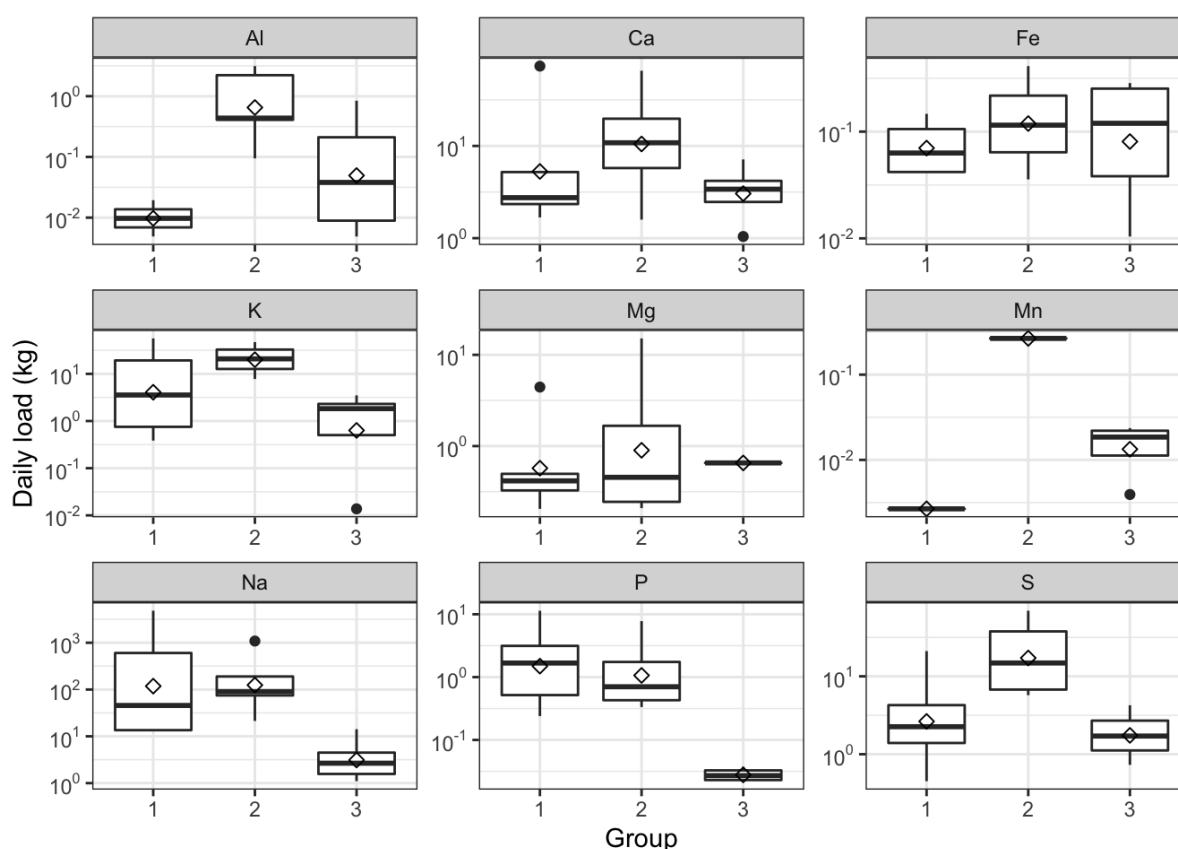

Figure 44 Daily loads of selected inorganic/metallic species monitored in each of the three industrial groups (1 = biopharmachem, 2 = food/beverage, 3 = waste management)

The recovery of components of TE for use in products such as fertilisers represents one opportunity for the management of TE. The prices of fertiliser products in Ireland are published by the Irish Central Statistics Office, and this information can be useful in assessing the costs and benefits of one form of recovery (Table 33). Note that many fertilisers are sold as composite blends of nitrogen (N, elemental), phosphorous (P) and potassium (K). Fertiliser blends are described by a three component ratio (N:P:K). For example "Compound 10-10-20" indicates that 10 % of the products weight is nitrogen, 10 % of the product is phosphorous, and 20 % of the products weight is potassium.

Table 33 Yearly average prices of fertiliser products (per 1000 kg) in Euro for the 2015 to 2020 period in Ireland (Source: Irish Central Statistics Office ("CSO Quicktables: Agriculture - Fertiliser Price," 2020))

Fertiliser	2015	2016	2017	2018	2019	2020
Ammonium Sulphate Nitrate (26%)	354	296	-	-	-	285
Calcium Ammonium Nitrate (27.5% N)	320	257	240	266	280	249
Compound 0-10-20	408	387	360	362	384	372
Compound 0-7-30	413	391	362	366	387	374
Compound 10-10-20	451	402	381	394	415	379
Compound 14-7-14	431	377	356	371	393	367
Compound 18-6-12	418	366	342	362	381	351
Compound 19-0-15	400	350	312	336	356	330
Compound 20-4-10	421	354	332	353	372	349
Compound 24-2.2-4.5	390	332	305	324	348	313
Compound 24-2.5-10	433	371	350	375	392	360
Compound 25-4-0	407	351	326	340	360	331
Compound 27-2.5-5	424	362	341	366	383	350
Granular Superphosphate (16% P)	419	-	-	-	-	373
Muriate of Potash (50% K)	418	390	365	366	388	367
Sulphate of Ammonia (21%)	336	280	271	284	-	-
Urea (46% N)	410	351	348	355	372	344

Conclusions

The variation in annual TE volumes for the biopharmachem, food/beverage and waste management sectors was assessed by analysing company flow data and publicly available AER data. The food/beverage sector was found to release significantly larger amounts of TE to sewer networks compared to the biopharmachem sector, although some biopharmaceutical companies also output substantial amounts of TE depending on the scale and nature of their operations. The waste management sector was found to output the lowest quantities of TE to sewer networks compared to both the biopharmachem or food/beverage sectors. This suggests that there are

substantial differences in the usage of water and the production of TE at waste management sites compared to other two sectors. Rainfall data corresponding to each site was compared to the annual volumes of TE generated by each company. The present data suggest that rainfall did not impact the levels of TE generated by the three sectors of industry assessed in this report. TE flow measurements at the point of release remain as the most important indicator for real-time monitoring of sewer inputs. Presently TE flow measurements are carried out by all industry sites releasing to sewer networks, however this data is not available to sewer operators or downstream wastewater treatment plants in real-time. It could be valuable to incorporate company flow data into an online dashboard to provide real-time information on TE releases to sewers, which may be useful for assessing sewer capacities and impacts on downstream wastewater treatment plant infrastructure.

The annual and daily loads of nutrient, inorganic and metallic species from TE to sewer networks were calculated based on annual emissions. The biopharmachem, food/beverage and waste management sectors contribute a range of species to sewer networks that could be of interest for recovery, either at the industrial input level or downstream at wastewater treatment plant level. The data indicates that the annual volumes of TE emitted by the biopharmachem and food/beverage sectors were significantly larger than the levels outputted by the waste management sector. The annual loadings of organic, inorganic, nutrient and metallic species emitted to sewers by industry were modest. Average outputs of total phosphorous (TP) were 600 kg/y for the biopharmachem sector, 2400 kg/y for the food and beverage sector and 10 kg for the waste management sector. Average outputs of total nitrogen (TN) were 800 kg/y for the biopharmachem sector, 2500 kg/y for the food and beverage sector and 850 kg/y for the waste management sector. These amounts of nutrient species are unlikely to offer significant economic value for industry to implement TE recovery technologies without additional incentives, or the need to further reduce levels of these parameters for license compliance reasons. This is in part due to the modest levels of these species, and the requisite economy of scale required to justify the installation of recovery technologies. Furthermore it is essential that the form of recovered nutrients must be of sufficient quality to allow it to be utilised for the desired applications without the need for additional costly processing.

An important caveat to these findings is that many of the companies included in the study were utilising removal technologies to control the levels of species in their TE prior to release to sewers. For example, the food/beverage sector commonly employs filtration, sedimentation, dissolved air flotation technology and biological reactors to reduce the amounts of particulates, organics and inorganics in their TE. Assessments of the viability of recovery technologies could be performed

on untreated TE by individual industries so that yields of recovered materials can be maximised to enhance value where an appropriate business case can be made.

4

Deployment of passive sampling and sensor technologies

Deployment of passive sampling and sensor technologies

Introduction

The deployment of passive sampler and sensor technologies is an objective of the project with the goal of improving the quality of information on the variation of TE over time as well as providing capacity for real-time monitoring of TE properties. Based on the TE composition that was established in section 3 of this report, companies were grouped into types for passive sampler and sensor parameters. The biopharmachem sector can be divided into two segments: biopharmaceuticals and pharmaceutical products. Biopharmaceutical companies produce biologically derived drugs, such as insulin and immuno-antibody treatments. Companies in type two are focused on the production of small molecule pharmaceuticals drugs, such as acetaminophen and ibuprofen, using industrial chemistry processes. The second sector of interest included both food and beverage producers. The food class in this study process a wide variety of animal derived products, including: meat, yogurt, and cheese. The beverage type of industries produce both alcoholic and non-alcoholic beverages such as beer, cider, soft drinks, energy drinks, milk and other dairy-type beverages. The waste management class was divided into companies that process commercial and industrial waste, and landfill sites that generate leachate. Passive sampler (PS) and sensor deployments were focused on TE sites that were characteristic of particular company types that had interesting variability in TE parameters. The feasibility of passive sampler and sensor deployments at each site was also assessed concurrently, as some sites utilised closed TE systems that did not have opportunities for the deployment of PS equipment without substantial modification of on-site infrastructure, which was outside the scope of the present research project. For example, it was preferred to perform deployments in continuous flows at the point of release to ensure that data collected is representative of a site's TE emitted to sewer, rather than deploying equipment at locations such as balancing tanks which are potentially static in composition for extended durations.

From the analyses completed on TE samples (nutrient, wet chemistry, anions, metals, and organics) a number of sites revealed characteristics of particular interest for monitoring via sensor and passive sampler technologies which are summarised in Table 34.

Table 34 Site parameters of interest for passive sampler and sensor deployments

Sector	Site ID	Parameters of interest
Biopharmachem	1	COD, TP, phosphate, organics
	2	COD, TP, TN, organics
	3	COD, phosphate, organics
	4	COD, TN, organics, turbidity
	5	COD, TN, ammonia, turbidity, organics
Food/beverage	6	Ammonia, nitrate, organics, sodium, chloride
	7	COD, TOC, TN, TP, turbidity, organics
	8	COD, TN, inorganics, organics, turbidity
	9	UV-vis absorbance, inorganics, organics, turbidity
	10	TN, organics
Waste management	11	TN, turbidity, organics, inorganics
	12	TN, ammonia, organics, inorganics
	13	Organics
	14	Ammonia, TN, organics
	15	Organics, ammonia

Based on the TE features outlined in Table 34, the most pressing targets for passive sampling were;

a) Organics such as those derived from COD, TP and TN contributions (both polar and non-polar in nature);

b) Inorganics such as nitrates, ammonia, phosphate, iron and aluminium; and,

c) Particulates as quantified using TSS and turbidity.

The following passive sampler phases and sensor technologies were selected for evaluation due to their capabilities in monitoring the aforementioned parameters;

a) The non-polar octadecyl (C_{18}) Chemcatcher for sampling of non-polar organics

b) The Hydrophilic-Lipophilic Balance (HLB) Chemcatcher for sampling of polar organics

c) The anionic Chemcatcher extraction phase for inorganic species; and,

d) Turbidity and conductivity sensors

Sensor and passive sampler deployments

Sensors

Two integrated sensor platforms (sondes) were utilised for the present study. Both sondes were YSI Exo3 platforms (Figure 45) purchased from Carl Stuart Ltd (Carlow, Ireland). These sondes could accommodate up to four multiparameter sensors and a centralised automatic wiper unit to remove fouling from sensor surfaces to facilitate long term unattended monitoring of TE. Each sonde included data collection capabilities and internal power packs to facilitate on-site

deployments without the need for connection to mains electricity or external data logging equipment. Sonde 1 was configured with a pH electrode, temperature, depth, conductivity, dissolved oxygen (DO) and turbidity sensors. Sonde 2 was configured with a pH electrode, temperature, depth, conductivity, turbidity and oxidation reduction potential (ORP) sensors.

Figure 45 YSI Exo3 sonde equipped with four sensors including optical dissolved oxygen, conductivity, temperature, fluorescent dissolved organic matter, depth and a centralised automated wiper

Passive samplers

Chemcatcher PS devices (receiving membranes and diffusion limiting membranes) and sampling equipment (cages and holders) were purchased from T.E. Laboratories Ltd (Carlow, Ireland). PS devices are constructed from three components: the membrane holder (comprised of a support disk, retaining ring and transport lid, Figure 46), a receiving membrane (Figure 47), and a diffusion limiting membrane.
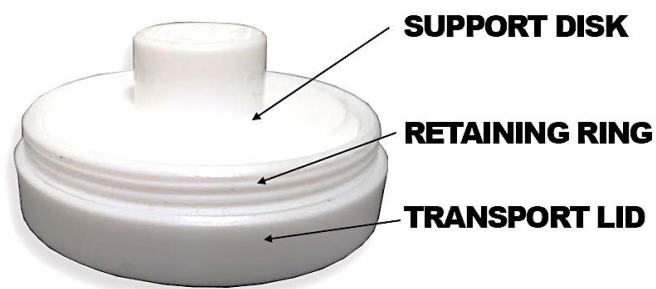
Figure 46 Chemcatcher holder showing the three components assembled. The support receiving phase membrane is placed on the support disk, and a diffusion limiting membrane is placed on top of this receiving disk. The retaining ring is used to immobilise the receiving and diffusion limiting membranes on the support disk. A transport lid is then used to cover the exposed diffusion limiting membrane prior to deployment

Figure 47 Image of a Chemcatcher Anionic-SR receiving membrane (47 mm diameter)

Three PS Chemcatcher configurations were evaluated at project sites as detailed in Table 35.

Table 35 Chemcatcher configurations showing receiving phases, diffusion limiting membranes, membrane sizes and targeted compounds for each passive sampler setup. PES = Polyether sulfone, LDPE = Low density polyethylene

Receiving membrane	Diffusion limiting membrane	Size (mm)	Targeted compounds
Oasis hydrophilic lipid balance (HLB)	PES	52	Polar organic
Empore C_{18} reversed phase	LDPE	47	Non-polar organic
Empore Anion-SR	-	47	Nutrients, anionic species

Prior to deployment, PS membrane holders were soaked for 24 h in a mixture of 10 % Decon-90 surfactant dissolved in deionised water. Following this, the PS holder components were rinsed with distilled water and then ultrasonicated in HPLC grade acetone (Sigma Aldrich, Ireland) for 10 min. The components were then rinsed with deionised water and allowed to air dry before being assembled with the requisite receiving phase and diffusion limiting membranes.

Oasis HLB receiving membranes were conditioned on a vacuum filtration manifold by rinsing the membrane with 50 mL of methanol, followed by 50 mL of deionised water, being careful to ensure that the membrane did not become dry during the conditioning process. PES diffusion limiting membranes were soaked in LC-MS grade methanol (Sigma-Aldrich) for 24 h prior to use and then allowed to air dry. Oasis HLB Chemcatcher's were then assembled using the PS holders and PES diffusion limiting membranes and stored in a refrigerator (4 °C) prior to deployment.

Anion-SR Chemcatcher disks (Figure 46) were conditioned with 15 mL of methanol on a vacuum manifold, after which an additional two aliquots of deionised water were used to complete the conditioning procedure, ensuring that the disk did not become dry during the conditioning process (Knutsson et al., 2013). Anion-SR membranes did not utilise a diffusion limiting membrane for the present deployment. Anion-SR receiving disks were mounted in Chemcatcher PS holders, wetted with 1 mL of deionised water, capped with a transportation lid, and stored in a refrigerator (4 °C) prior to deployment.

Non-polar C_{18} Empore receiving membranes were soaked in LC-MS grade methanol (Sigma Aldrich) for 24 h before prior to conditioning on a vacuum manifold with 50 mL of methanol, followed by 150 mL of deionised water. The C_{18} receiving phases were then dried on the vacuum manifold using air over a period of 30 min. The C_{18} receiving membranes were used with LDPE diffusion limiting membranes. LDPE membranes were soaked in *n*-hexane over a period of 24 h prior to use, after which they were air dried. To assemble the non-polar C_{18} Chemcatcher, the C_{18} membranes were wetted with 1 mL volume of HPLC grade *n*-octanol and acetone (45:55) (Sigma-Aldrich, Ireland). The receiving phase was then assembled in a Chemcatcher housing with a LDPE diffusion limiting membrane placed over the wetted Empore C_{18} receiving phase. The C_{18} Chemcatcher holders were sealed using transportation caps and stored in a refrigerator (4 °C) prior to deployment.

Site selection and deployments

In the biopharmachem sector it was important to sample sites that comprise both pharmaceutical and biopharmaceutical type TE. Site 4 produces biopharmaceuticals that could be grouped with

sites 1 and 2 in terms of TE properties. Site 5 however produces pharmaceutical products more typical of site 3. Both Sites 4 and 5 had opportunities for deployment in continuous streams of TE that are appropriate for the deployment of PS and sensor equipment. The food and beverage sector was best represented by three types of companies undertaking either food processing of meat or dairy products or beverage production either dairy, or other beverages. To achieve good deployment coverage of this sector, site 8 (non-dairy beverages), site 9 (food), site 10 (dairy/beverages) were selected for deployments based on the TE profiles and accessibility of these sites for deployments. Waste management sites were grouped into two classes either from waste processing facilities (Sites 11 and 12) or landfill leachate management (sites 13, 14, 15). Due to the primary focus of the project being to characterise TE directly released to sewer, the waste processing facilities were selected for deployments as the landfill sites included in the study were not releasing TE to sewers.

Table 36 lists the passive sampler deployments that were completed during this project. Presently this selection gives excellent coverage using 3 different passive sampler phase types.

Table 36 Passive sampler deployments completed, and their durations. NC = not completed

Sector	Company ID	Deployed sampler	Deployment duration (d)
1	4	Polar organics	20
1	4	Nutrients	20
2	9	Polar organics	11
2	9	Nutrients	11
2	10	Non-polar organics	8
2	8	Non-polar organics	8
3	11	Polar organics	9
3	11	Nutrients	9
3	12	Nutrients	NC
3	12	Non-polar organics	NC

Impact of COVID-19 on sensor and passive sampler deployments

Due to the impacts of COVID-19 in preventing access to sites and to the university laboratories, limited sensor deployments were completed. However, from the data generated from real-time monitoring at the selected sites, valuable information has been achieved. A summary of this data is shown in the Appendix. At the sites, uninterrupted measurements were collected on temperature, dissolved oxygen, conductivity, pH, salinity, and turbidity.

The results shown in the figures illustrate the ability to observe rapid changes in turbidity and conductivity that can inform the company on changes occurring at the site. These variations may be due to process changes. By carrying out trend analysis and event monitoring, it would be possible to identify unusual or unexpected changes to effluent composition. The latter could then lead to a more directed analysis. This promising set of data in this project informs the need for further research on real-time data collection at sites where logistically possible, to enable event analysis and establishment of alarms for TE monitoring.

Because of COVID-19 restrictions, Dublin City University's research laboratories were closed thus preventing the analysis of passive sampler materials that were deployed at each of the industry sites described in Table 36. However, this project has highlighted the types of passive samplers that are most suited to each TE site and also, the procedures for deployment have been optimised. These experiences can now be translated to any further work.

5

Identification of surrogate species for monitoring TE properties

Identification of surrogate species for monitoring TE properties

Introduction

TE emissions from industry impact the composition of effluent in sewer networks in a more variable manner than wastewaters derived from commercial, urban or rural sources due to the vast range of operations performed by industry. As a result, the emissions of TE from industry are regulated by environmental protection agencies and water utility companies to ensure that sewer integrity is maintained. TE emissions licenses consider the capacity of surrounding wastewater treatment infrastructure that process TE along with other wastewaters, since it is essential that these facilities are able to provide sufficient capacity for wastewater treatment (Prasse et al., 2015). While wastewater treatment plants are well optimised for processing commercial, urban and rural wastewater, the unique compositions of industrial TE can present a challenge to wastewater treatment plant operation in some cases (Dsikowitzky and Schwarzbauer, 2014). For example, the emission of high levels of ammonia containing compounds can impact sewer health, generate undesirable odours and furthermore detrimentally impact wastewater treatment processes (Barczak and Kulig, 2017).

Presently, TE monitoring is reliant on grab and composite sampling to determine the composition and loadings of TE. These samples are often submitted for analysis at commercial laboratories with analytical turnaround times between 1 to 7 days depending on the parameter being measured. This requirement to collect, preserve, transport and analyse volumes of TE introduces a delay period between the time of sampling and the acquisition of an analytical result, which limits the ability of a company to control the properties of their TE emissions. Some progress towards the development of online TE analysers for TOC, COD, TN and TP, phosphate have been made, however the capital and operational costs of these technologies are considerable. Two alternative technologies to process analyser technologies are sensors and passive samplers (PS) which have some useful capabilities for informing TE composition (Charriau et al., 2016; Qin et al., 2012). Sensors are already utilised for the measurement of temperature, pH and flow volumes by some industries. There are a range of sensor technologies including, turbidity, conductivity ion selective electrodes (ISEs), electrochemical and spectrophotometric sensors that are potentially of value to deliver real-time information on TE composition. PS technologies provide a new and selective method of performing composite sampling of targeted species in water, while reducing the need to preserve and transport large volumes of samples. PS devices function by adsorbing dissolved organic, inorganic and metallic species from TE over a deployment duration, thereby providing a composite average of compound loadings emitted by a site.

The aim of this research project was to identify markers or surrogate parameters that could be used for monitoring TE. This was achieved by characterising TE samples that are representative of three industrial categories, (i) biopharmachem, (ii) food/beverage and (iii) waste management industries. TE was analysed with a range of standard analysis techniques including wet chemistry, chromatographic, sensor and spectroscopic measurements. The data obtained from this characterisation sought to identify the levels of organic, inorganic and metallic species in TE to determine which parameters could be utilised as surrogates for TE properties. Sensor measurements such as turbidity and conductivity along with ion selective electrode technologies and other chemical analysis techniques were evaluated for purposes of monitoring TE composition.

Methods

TE samples were obtained from each of the project sites and analysed as described in section 3 and passive sampling and sensor deployments are discussed in section 5. The data sets obtained were analysed for relations between various TE parameters using the R software package (version 3.6.2) and the RStudio Integrated Development Environment (version 1.2.5033). Data visualisation was performed using the ggplot2 package, linear modelling was performed using the modelr and broom packages, principle component analysis was performed using factoextra and FactoMineR, correlation analysis was visualised with the corrplot and ggpairs package.

Results and discussion:

Analysis of properties of TE using principle component analysis

Due to the large number of parameters measured on TE samples obtained from the project sites, data reduction techniques were required to provide insight into which parameters are the most describing TE variation across the three sectors of interest. Principal component analysis (PCA) was used to determine links between sensor measurements and the chemical analysis performed. PCA provides a robust means of summarising multivariate data that contains large number of interrelated parameters. For example, TOC measurements are correlated with COD measurements as both these parameters quantify types of organic carbon in a sample. PCA was performed on 25 variables including; ammonia, chloride, COD, conductivity, nitrate, nitrite, phosphate, sulphate, TN, TOC, TP, turbidity, aluminium, boron, calcium, iron, potassium, magnesium manganese, sodium, phosphorous, strontium, sulphur, vanadium and zinc. PCA was able to reduce the dimensionality of this dataset down to 8 components or dimensions as shown in Figure 48.

Scree plot
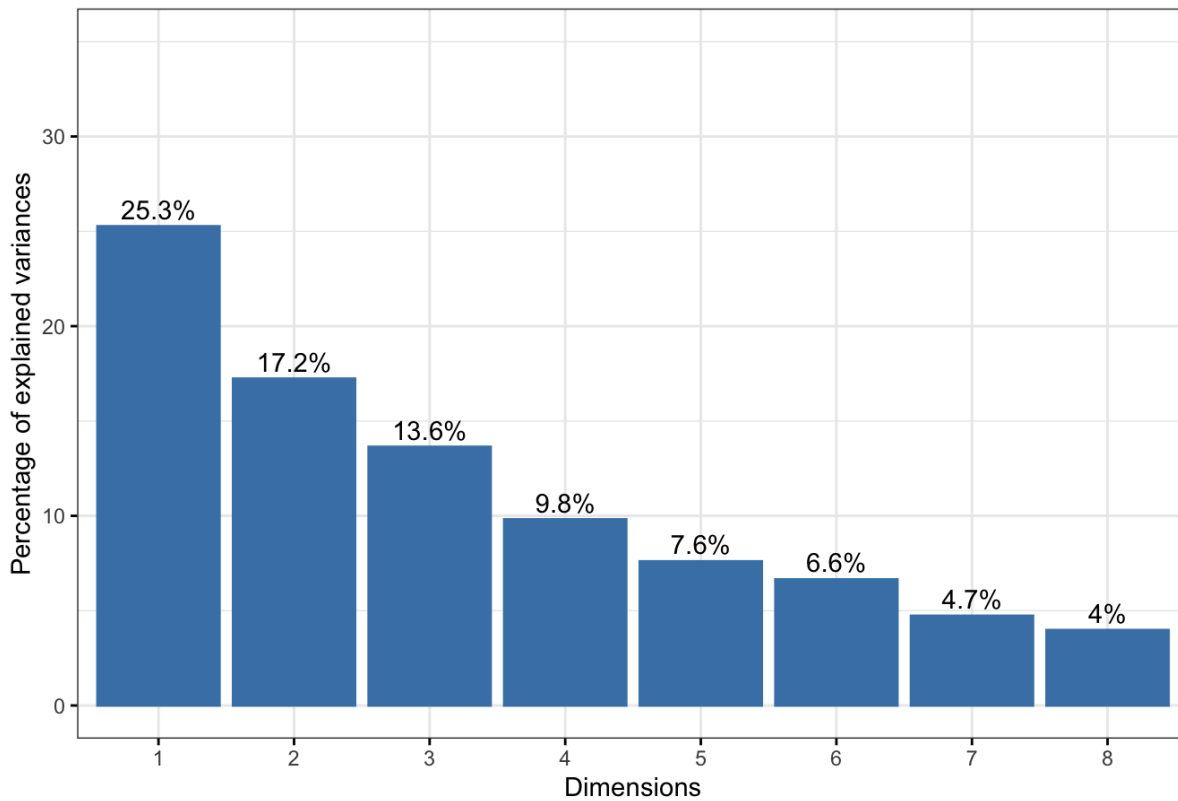
Figure 48 Scree plot showing the percentage of variance explained by the first 8 dimensions of the PCA

The first 8 principal component dimensions captured 90 % of the variance of all of the parameters, with the first 4 dimensions capturing 66 % of this variation in TE. Evaluation of the PCA can be used to classify samples as similar or different as shown in Figure 49 as well as provide insight into which parameters may be with one and other.
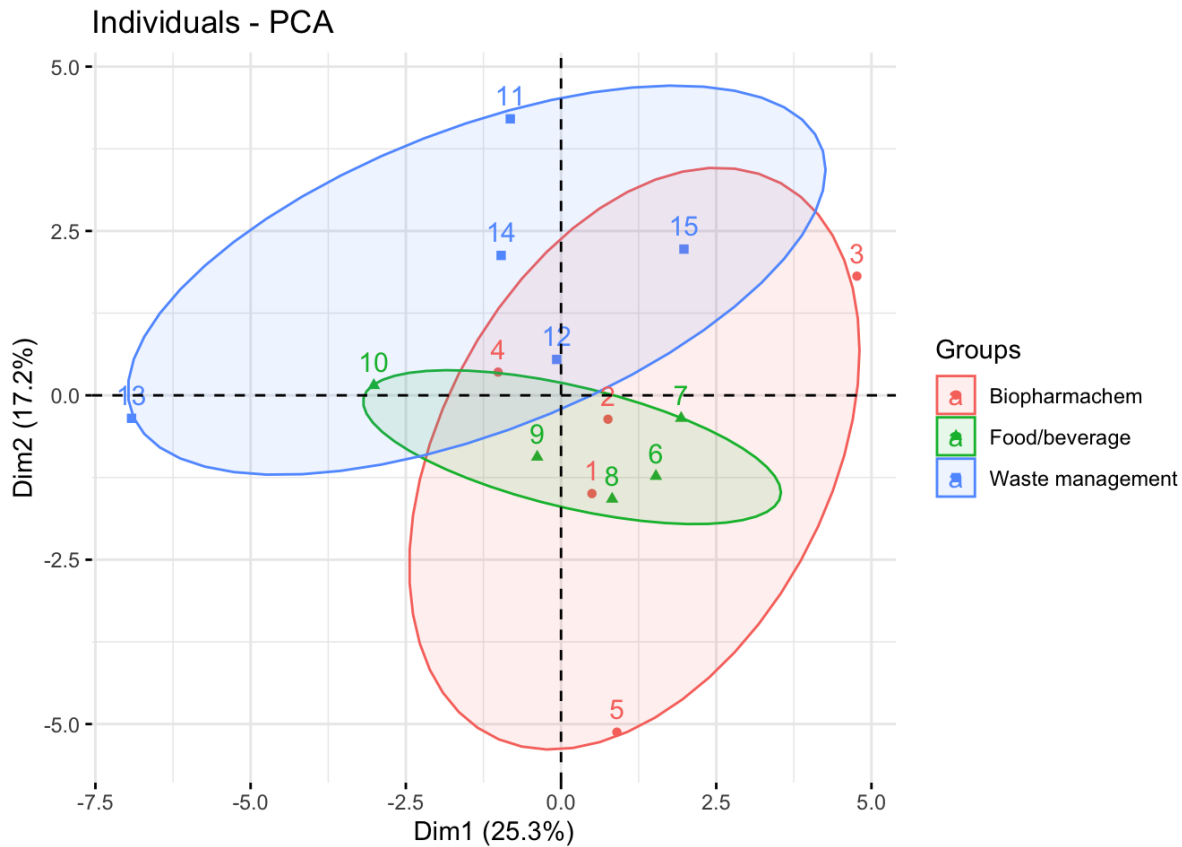
Figure 49 Classification of samples for PCA dimensions 1 (Dim 1) and 2 (Dim 2)

Of the biopharmachem sites evaluated sites 3 and 5 were substantially different in their properties compared to the other samples, as classified by PCA Dim1 and Dim2. Sites 3 and 5 were small molecule synthesising pharmaceutical companies, in contrast to sites 1, 2 and 4 of the biopharmachem group who were preparing protein-based drugs. Food beverage sites 6, 7, 8, 9 and 10 were grouped together on Dim1 and Dim 2 indicating similarities in these sites. Waste management site 13 was substantially different from all of the samples within the data set, while sites 11, 12, 14 and 15 were more similar to one and other within the sector.

The contribution of each parameter towards the first (Dim1) and second (Dim2) PCA dimensions is provided in Figure 50. This figure is useful for providing insight into the positioning of the different sites within the PCA visualisation space.

Figure 50 Variable contributions to Dim1 (x-axis) and Dim2 (y-axis) of PCA. Arrow length and colour are indicative of the strength (contrib) of the contribution to the two PCA dimensions

The percentage contribution of each measurement parameter towards Dim1 is shown in Figure 51, which captured 25.3 % of the datasets variation. Dim1 revealed that a combination of phosphorous, turbidity, chloride, conductivity, COD, TP, TOC, phosphate, calcium and zinc parameters are responsible for distinguishing TE from different sites. The link between organic parameters such as TOC-COD and phosphorous-phosphate along with chloride-conductivity-turbidity highlights the potential of surrogacy of sensor measurements of organic carbon and phosphorous species.

Figure 51 Contributions of variables to Dim1 of PCA. The red dashed line shows the average contribution of all parameters to Dim1

Contributions of variables to Dim2 are shown in Figure 52 which captured a total of 17.2% of the datasets variation. Metallic and inorganic species including sodium, sulphate, nitrite, iron, and conductivity were the main parameters contributing to the variation of Dim2. Surrogacy of the conductivity parameter for these inorganic species will be explored in the follow up sensor deployment sections of this report.

Contribution of variables to Dim-2

Figure 52 Contributions of variables to Dim2 of PCA. The red dashed line shows the average contribution of all parameters to Dim2

In general all sectors were clustered together which means that qualitatively the measurements did not distinguish sectors from one and other, however there was a significant amount of variation between individual samples (Figure 49). Out of the sites evaluated, site 13 was found to have very low levels of phosphorous and organic carbon species, which resulted in it being strongly separated on Dim1 from all of the other sites, while its levels of inorganic species were unremarkable. Sites 3 and 5 were both biopharmachem sites, however each was strongly separated by a different PCA dimension. Site 3 was distinguished by its high levels of organics/phosphorous (Dim1), and lower amounts of inorganic species, while site 5 indicated an unremarkable level of organics/phosphorous and high levels of sodium, with low levels of sulphate and nitrate accompanying this measurement (Dim2). The waste management site 11 had high levels of inorganic species, likely due to the untreated nature of leachate obtained from this site. The contribution of each parameter towards the third (Dim3) and fourth (Dim4) PCA dimensions is provided in Figure 53. This figure is useful for providing further information on the differences between sites.
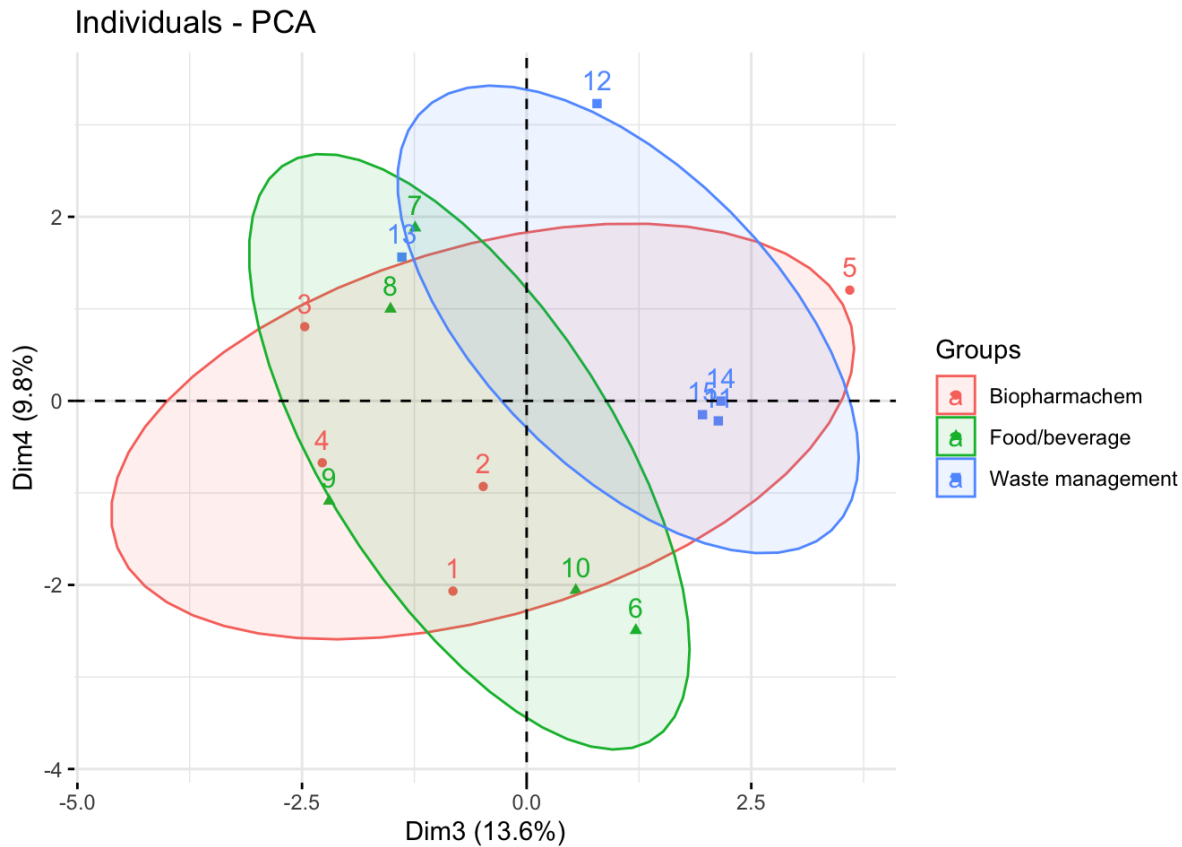
Figure 53 Classification of samples for PCA dimensions 3 (Dim3) and 4 (Dim4)

The percentage contribution of each measurement parameter towards Dim3 and Dim4 is shown in Figure 54, where these dimensions captured 13.6 % and 9.8 % of the variation respectively. Qualitatively Dim3 and Dim4 showed that the biopharmachem and food/beverage TE, other than that from site 5 were similar in composition. Site 5 was more similar in properties to a waste management site. This is likely due to a process being carried out at that particular site. Generally the waste management sites were distinguished from the biopharmachem and food/beverage sites based on PCA Dim3 and Dim4.
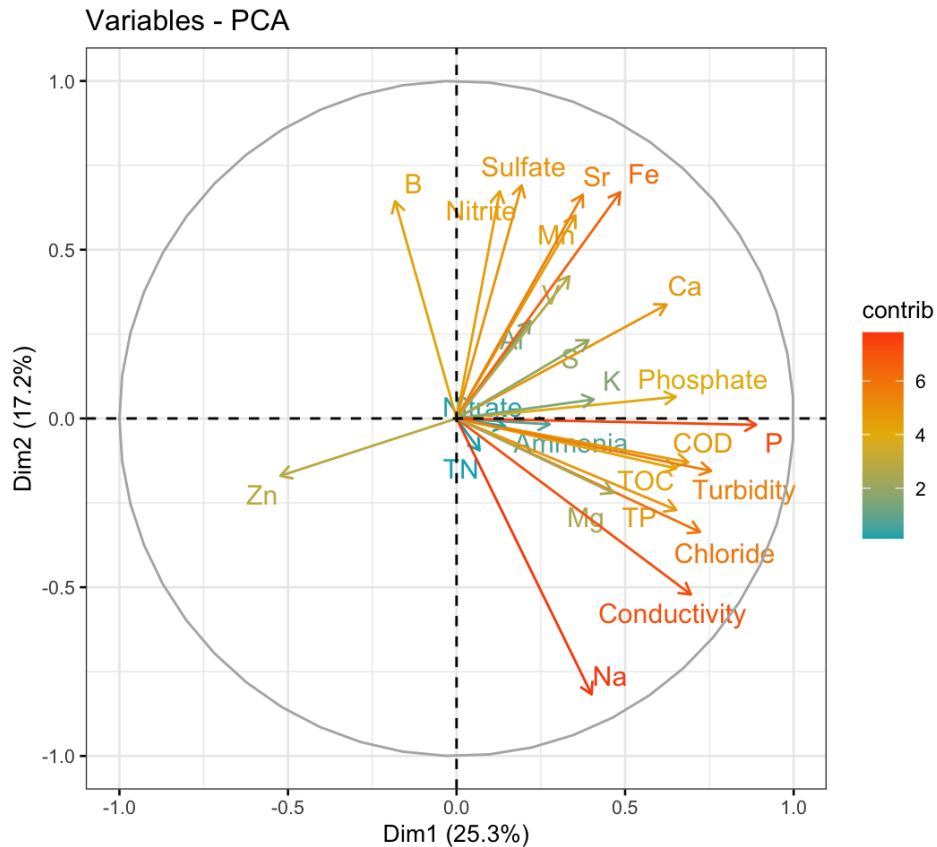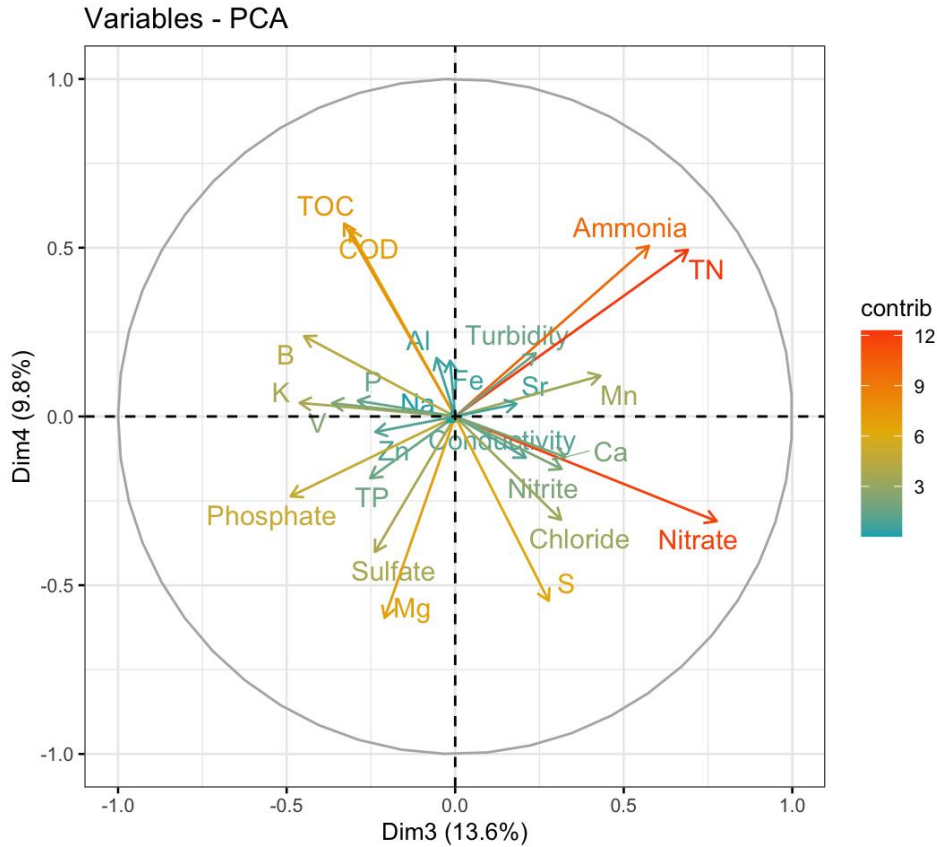
Figure 54 Variable contributions to Dim3 (x-axis) and Dim4 (y-axis) of PCA. Arrow length and colour are indicative of the strength (contrib) of the contribution to the two PCA dimensions

Specifically, Dim3 was linked to nitrate TN, ammonia, phosphate and potassium as shown in Figure 55. The top three parameters were all nitrogen containing species indicating that Dim3 is descriptive of overall nitrogen levels detected in TE. Site 5 had evidence for high levels of ammonia and TN which gave rise to its separation from other biopharmachem sites.

Contribution of variables to Dim-3
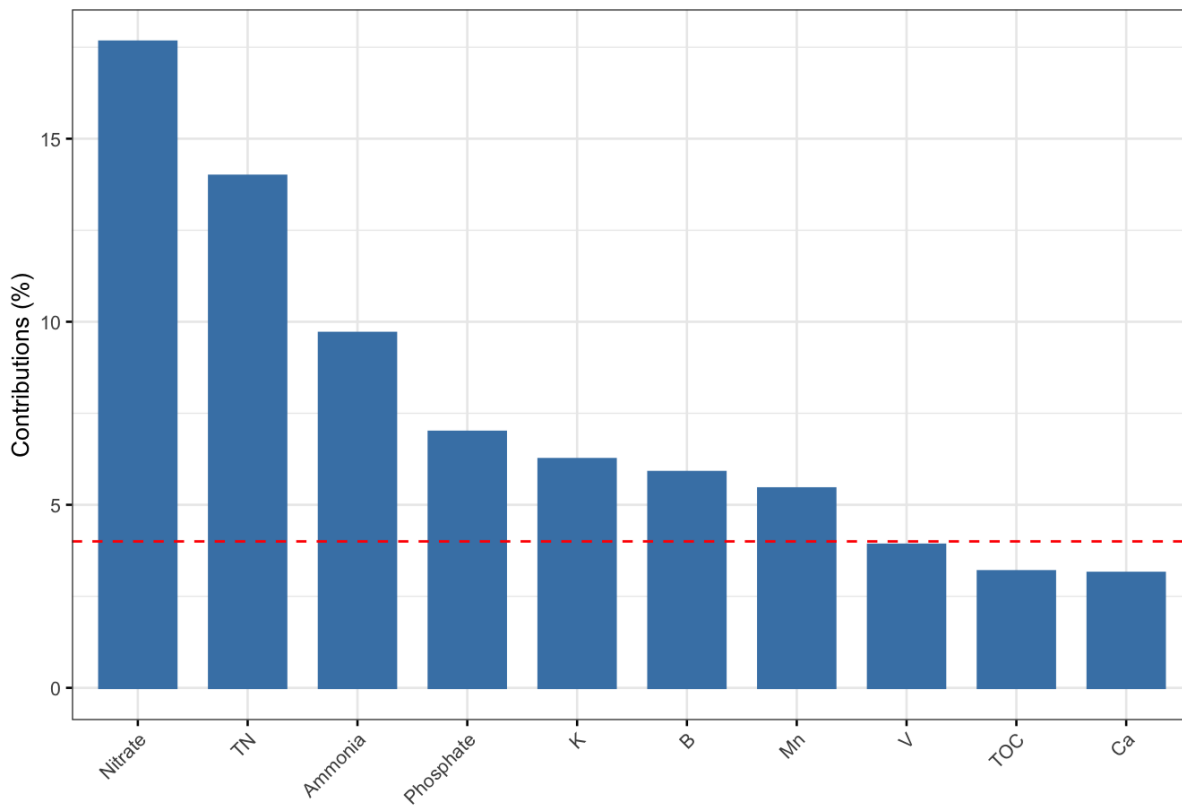
Figure 55 Contributions of variables to Dim3 of PCA. The red dashed line shows the average contribution of all parameters to Dim3

Dim4 PCA variation was caused by levels of magnesium, TOC, COD, sulphur, sulphate, ammonia and TN Figure 56. This composite parameter was descriptive of the total level of species present in TE from each site.
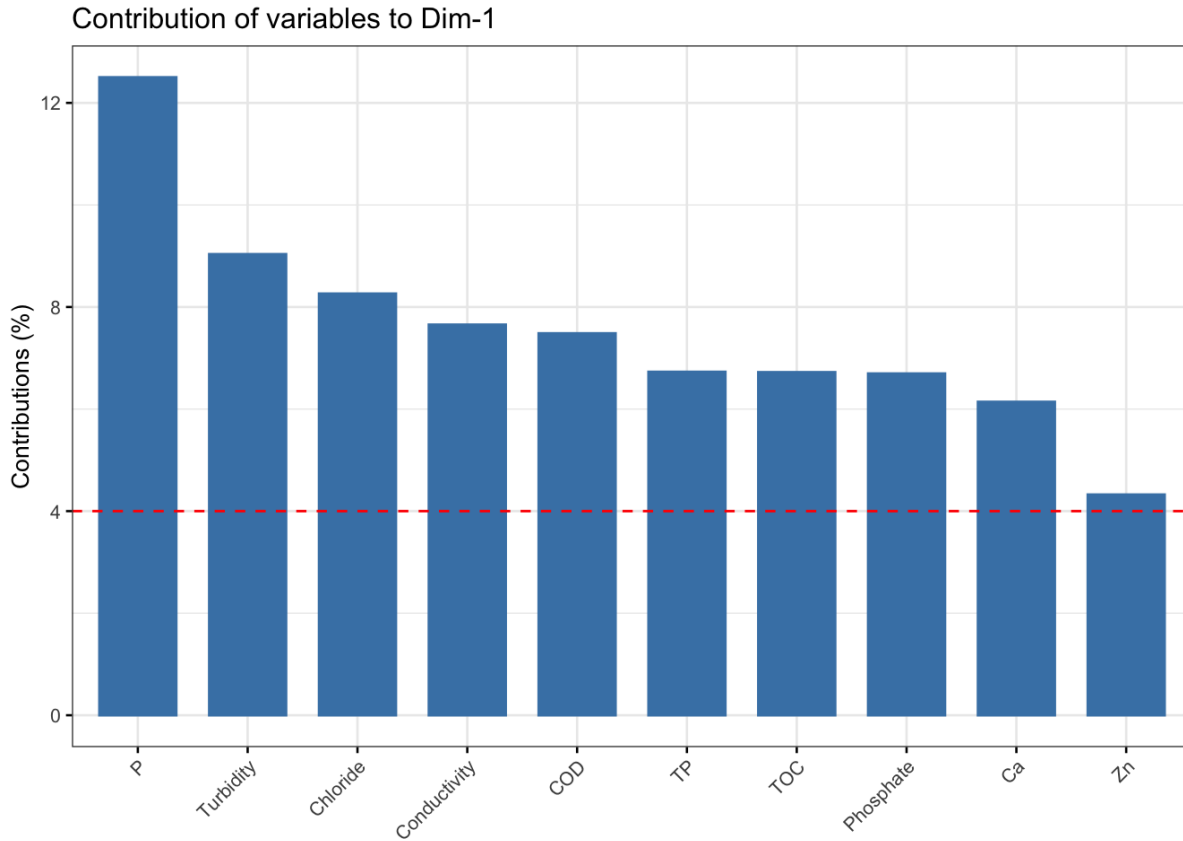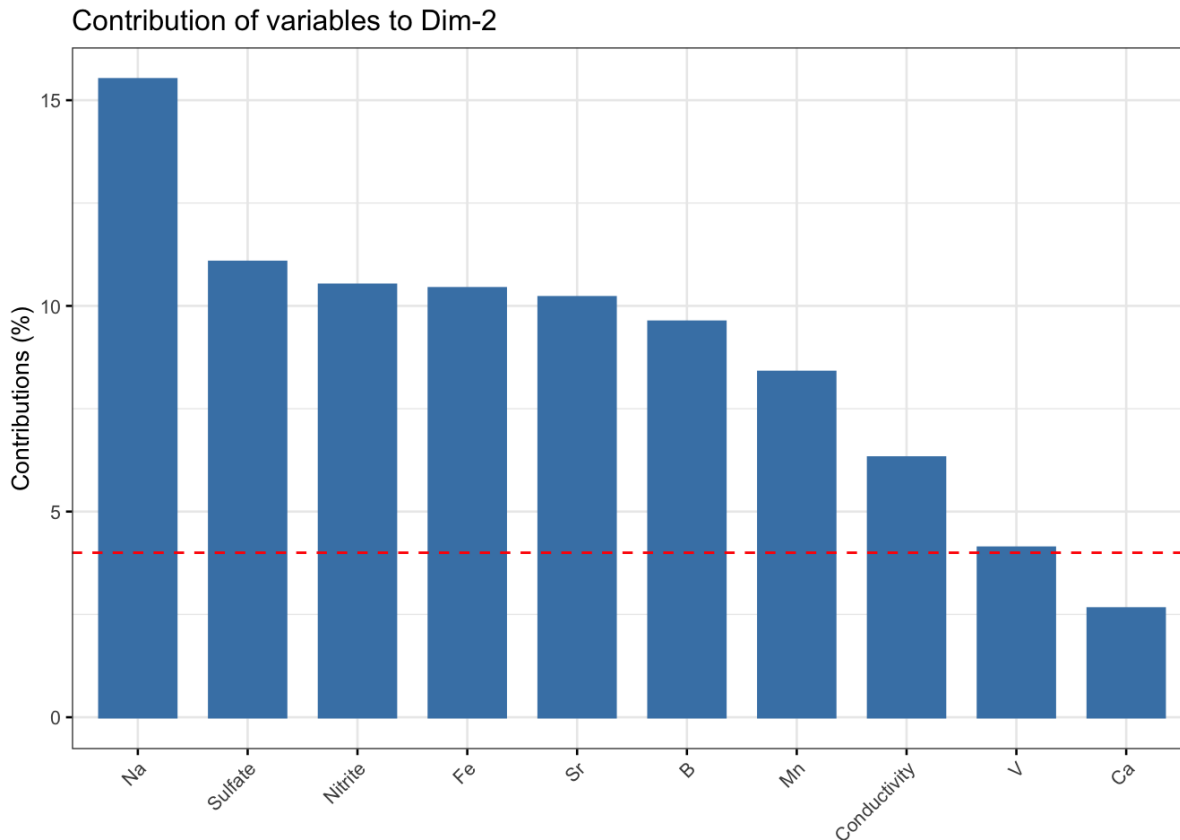
Contribution of variables to Dim-4
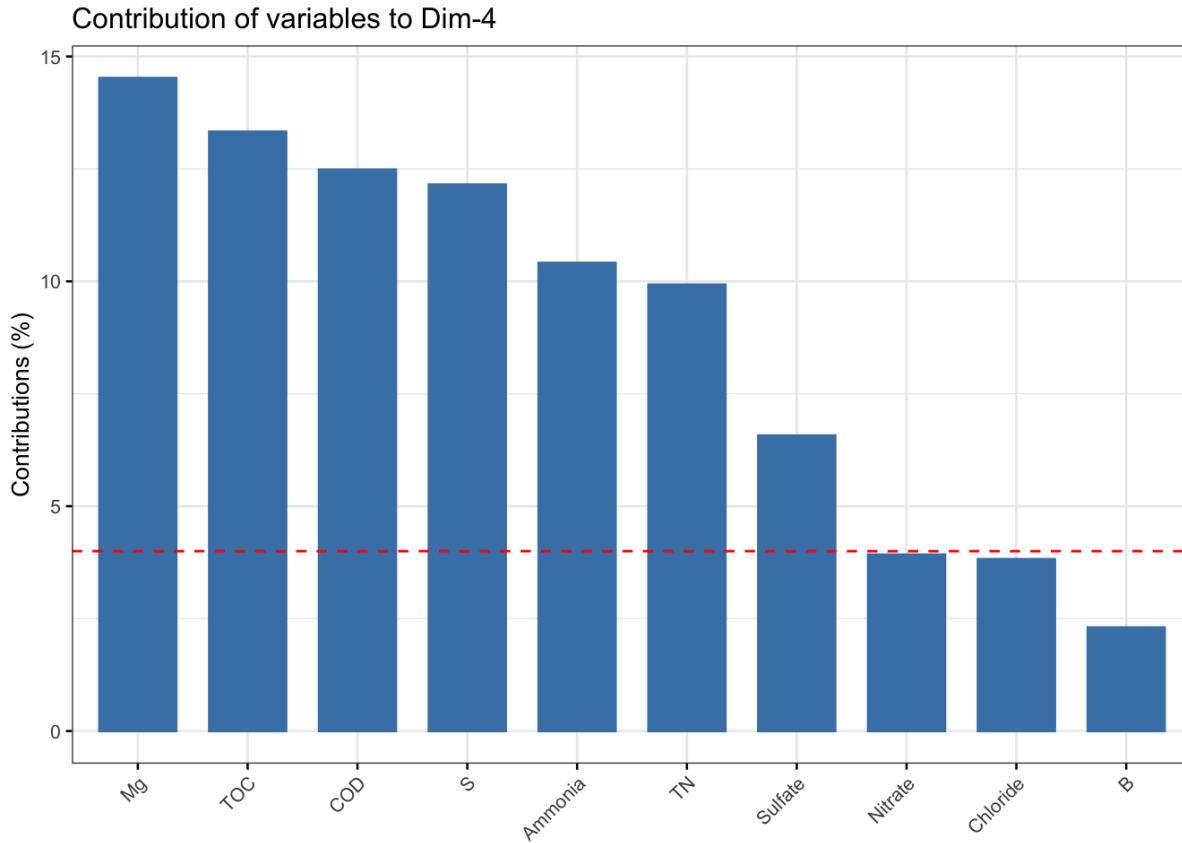
Figure 56 Contributions of variables to Dim3 of PCA. The red dashed line shows the average contribution of all parameters to Dim4

Nutrient and inorganic compound associations

Correlation analysis was performed between the nutrient and inorganic species that are monitored in TE licenses. The parameters ammonia, chloride, COD, conductivity, nitrate, nitrite, phosphate, sulphate, TN, TOC, TP and turbidity. These parameters where scaled logarithmically prior to analysis due to the wide ranges over which these the parameters varied. This allowed comparison between parameters that vary over multiple orders of magnitude. Figure 57 shows a heat map indicating the correlations between each of the measured parameters.
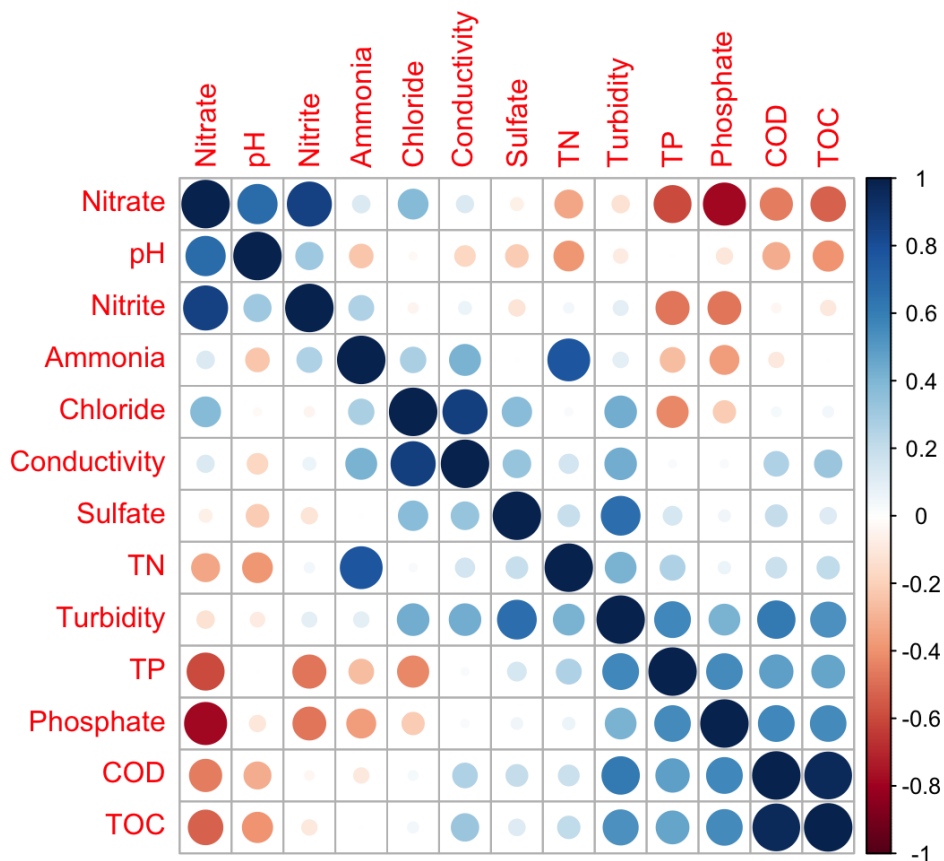
Figure 57 Correlation analysis of nutrient, sensor and selected inorganic parameters. Circle size and colour indicates the level of significance of a correlation, with blue coloured circles indicating positive correlations between parameters, light colours or blank cells indicate no correlation, and red circles indicating negative correlations between parameters

Nitrate and nitrite were correlated which is expected given the oxidation pathway of these species from organic nitrogen and ammonia sources. TN was similarly correlated with ammonia, which is expected as ammonia is an important degradation product from nitrogen containing organics such as proteins, furthermore ammonia levels in samples will increase TN measurements. Conductivity was strongly correlated with chloride readings which is anticipated due to the wide use of sodium salts and sodium hydroxide for pH balancing purposes at the industrial sites included in the study. Turbidity was weakly linked with the parameters of TP, phosphate, COD, TOC and sulphate. Similarly TP and phosphate levels were linked with each other. As expected COD and TOC were strongly correlated with each other as these assays measure fractions of organic carbon. Evaluating the statistical significance of these correlations was performed using a t-test at the 95% confidence level, with the results shown in Figure 58.
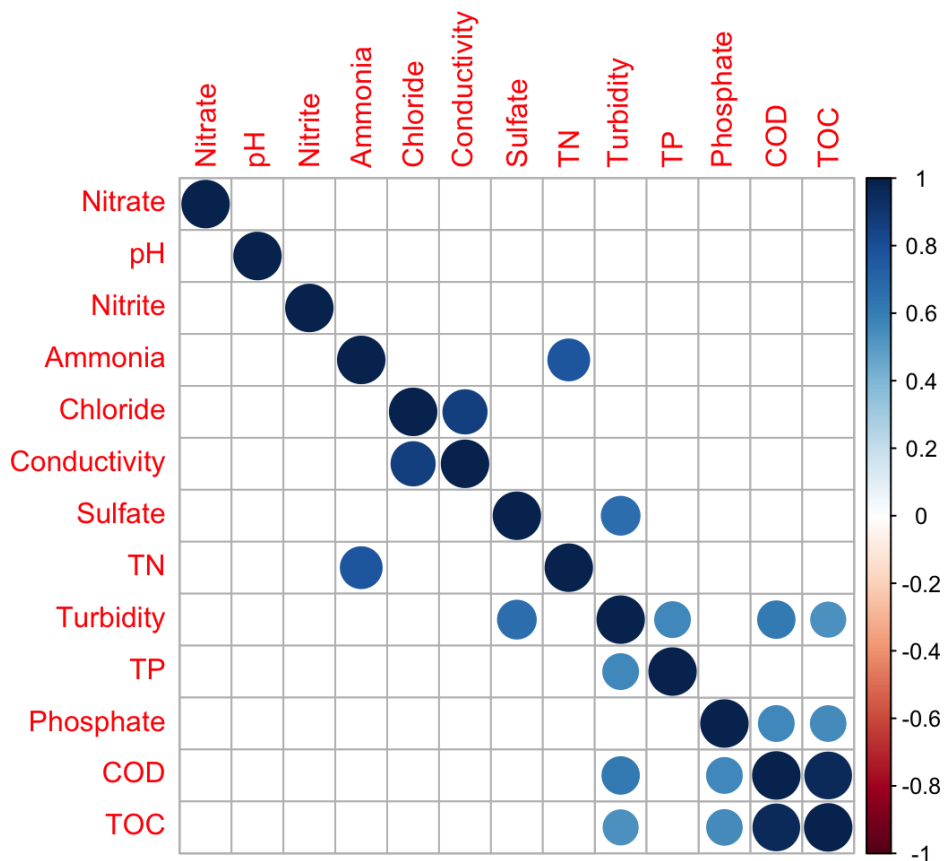
Figure 58 Correlations between nutrient, inorganic and sensor parameters, showing statistically significant correlations only (α = 0.05)

This confirmed the correlations between conductivity and chloride levels, TN and ammonia, turbidity and TP, as well as turbidity and COD-TOC. Additionally links between phosphate-COD-TOC were confirmed, similar to the PCA analysis performed in the previous section. These results suggest that turbidity, chloride and ammonia sensing electrodes may be valuable for monitoring these species in real-time. Expanding the analysis to compare spectroscopic properties of TE samples with nutrient parameters provided additional capacity for quantifying levels of organic and inorganic species in TE. Linear modelling was performed on the parameters with statistically significant correlations to determine whether sensors data on conductivity and turbidity could provide useful quantitative information on nutrient levels.
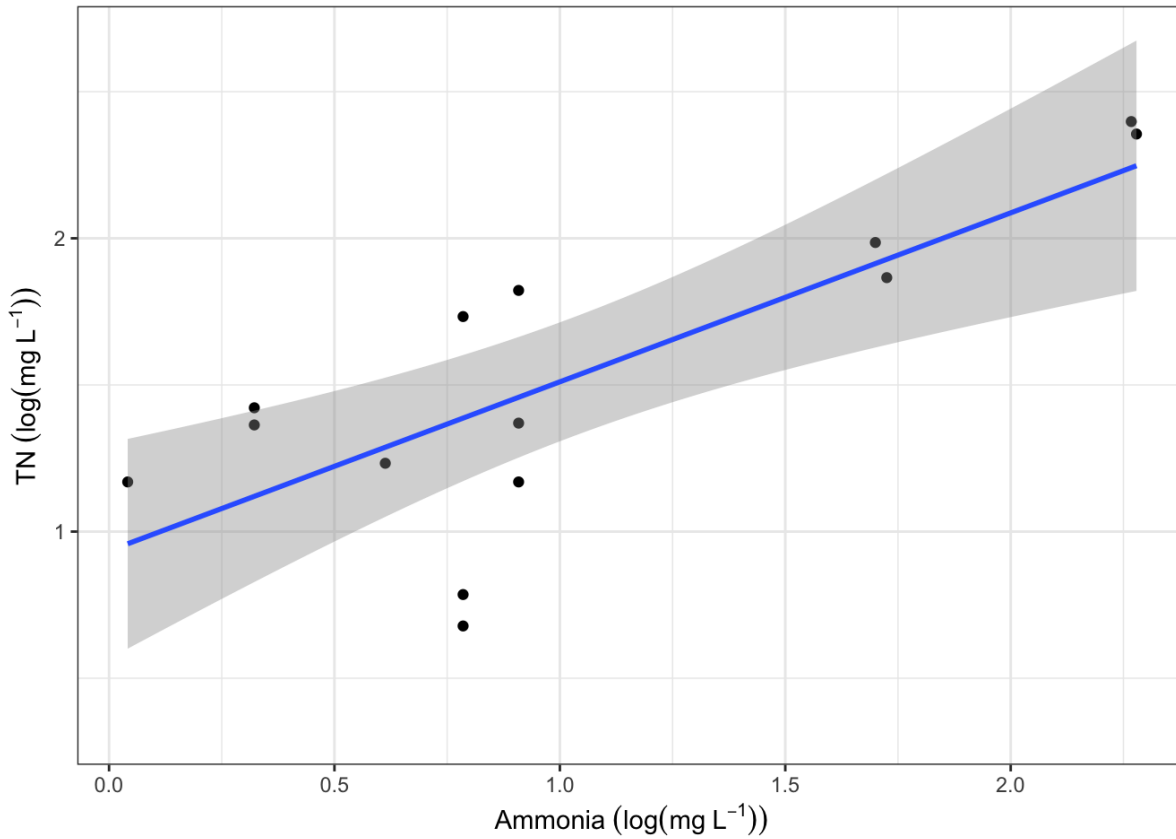
Figure 59 Linear regression of ammonia vs TN. Both parameters were log scaled prior to plotting. Adjusted R^2 = 0.56, p-value = 0.00125

The relation between ammonia and nitrogen is shown in Figure 59 which revealed a significant, but only mildly strong relation (adjusted R^2 = 0.56) between the two parameters. The wide confidence intervals on the linear relation indicate that there is substantial site-to-site variation necessitating consideration of specific site effects.
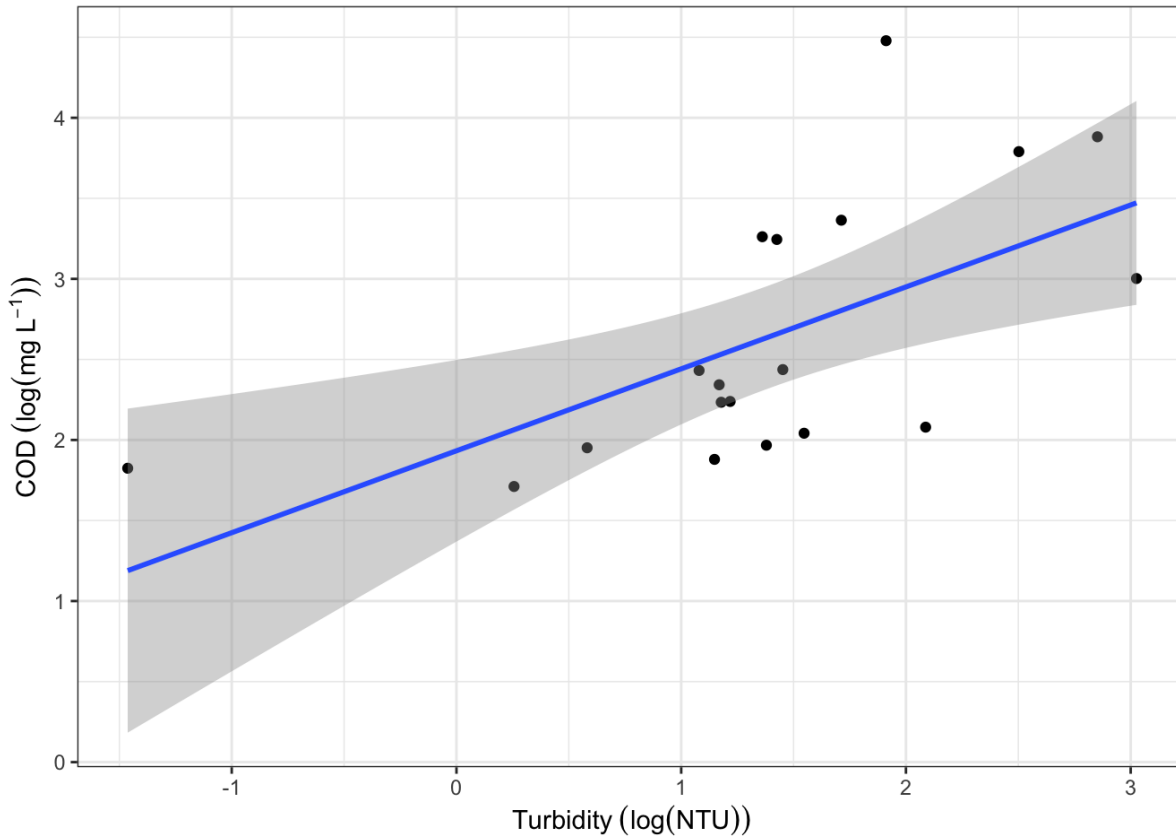
Figure 60 Linear regression of turbidity vs COD. Both parameters were log scaled prior to plotting. Adjusted R^2 = 0.377, p-value = 0.00513

Similarly the linear relationship between turbidity and COD is shown in Figure 60 was statistically significant, but weak in strength (adjusted R^2 = 0.377), highlighting the large variability in the data arising from the range of different types of TE sites. Evaluation of turbidity and TOC revealed a similarly significant but weak association between these two parameters (Adjusted R^2 = 0.290, p-value = 0.0174). Further evaluation turbidity data and COD measurements within specific sites or industrial groups would provide valuable insight into TE composition.
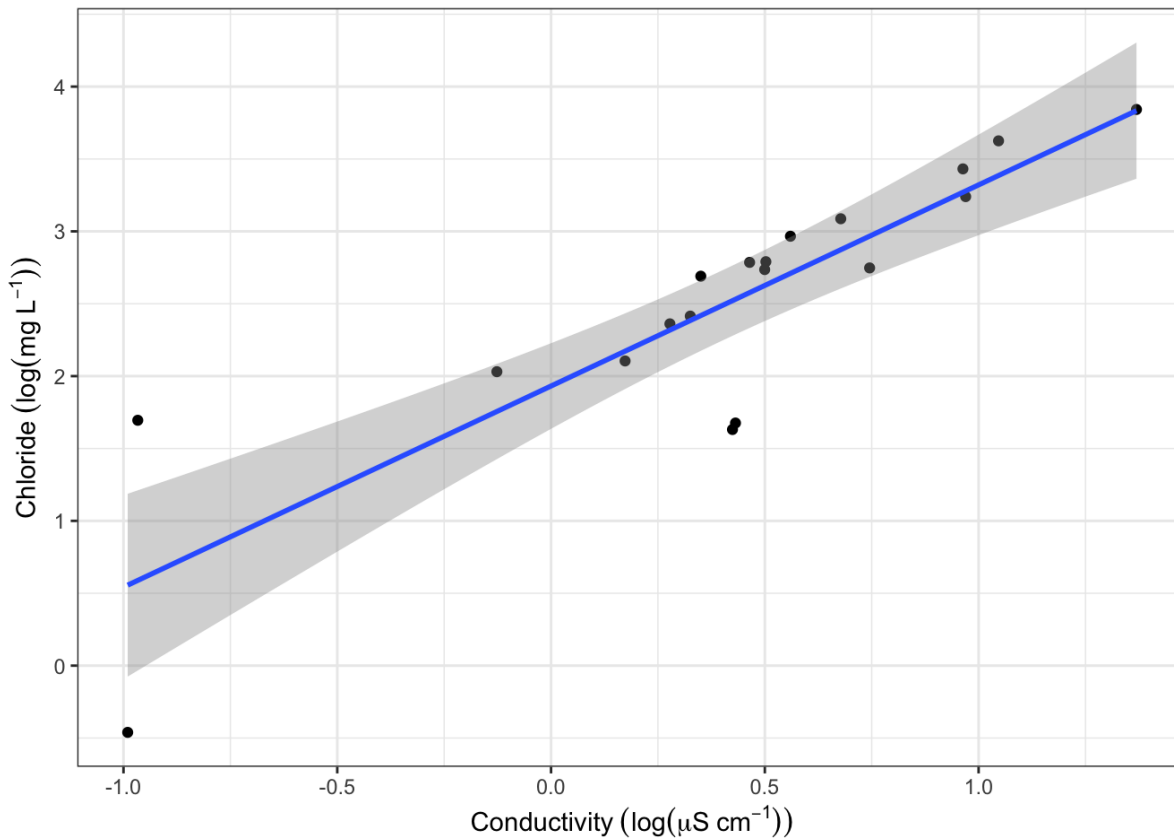
Figure 61 Linear regression of conductivity vs chloride. Both parameters were log scaled prior to plotting. Adjusted R^2 = 0.743, p-value = 2.1e-6

Regression between conductivity measurements and chloride levels revealed a significant link between the two parameters with a moderate association (R^2 = 0.743). This suggested that conductivity may serve as a useful surrogate for chloride levels, although the wide confidence intervals for the model again indicate that site specific TE analysis is required to confirm levels of chloride and calibrate conductivity sensors.

Metals and inorganic species

The concentrations of a selection of metals were measured using inductively coupled plasma optical emissions spectroscopy (ICP-OES). Correlation of these metals with one and other along with sensor and nutrient parameters was carried out to determine potential for surrogacy of sensors or nutrient parameters for monitoring levels metals in TE. The following metals were not detected in any of the TE samples collected: Ag, As, Ba, Be, Bi, Cd, Co, Cr, Ga, In, Li, Ni, Pb, Rb, Se, Te. Additionally, Cu, Mn, Sr, V and Zn where detected infrequently and these metals along with the non-detected metals were excluded from correlation analysis and linear modelling. Regression analysis indicated that there were significant associations between a number of parameters as summarised in Table 37.

Table 37 Summary of metals correlations with nutrient and sensor parameters

Metal/inorganic species	Detected (Yes/No /Infrequent)	Significant correlation (95%)	*p*-value	Adjusted R^2
Ag	No			
Al	Yes	No significant correlations		
As	No			
B	Yes	Ammonia	3.59E-02	0.707
Ba	No			
Be	No			
Bi	No			
Ca	Yes	No significant correlations		
Cd	No			
Co	No			
Cr	No			
Cu	Infrequent	Excluded		
Fe	Yes	No significant correlations		
Ga	No			
In	No			
K	Yes	Conductivity	2.10E-03	0.813
Li	No			
Mg	Yes	pH	2.42E-02	0.605
Mn	Infrequent	Excluded		
Na	Yes	Conductivity	1.50E-06	0.965
Ni	No			
P	Yes	TP	7.55E-04	0.846
Pb	No			
Rb	No			
S	Yes	Sulfate	1.08E-03	0.881
Se	No			
Sr	Infrequent	Excluded		
Te	No			
V	Infrequent	Excluded		
Zn	Infrequent	Excluded		

In general metal concentrations were not correlated with the nutrient or sensor parameters evaluated in this study, highlighting the importance of either measuring these species directly or utilising different sensor technologies. The strongest linear association was found between sodium and conductivity sensor measurements (R^2 value of 0.965), which is anticipated due to the common usage of salts during the production of a range of goods, or as a result of sodium

hydroxide base additions during pH balancing of TE prior to release. Similarly, potassium was also correlated with conductivity of TE samples to a lesser extent (R^2 value of 0.813) and this cation is also a commonly occurring light metal that is present in water and TE at lower levels than sodium. Sulphate was correlated with levels of sulphur which suggests that the use of sulphate ISE technologies may be used to directly monitor this species in TE.

Organics

Levels of volatile and semivolatiles organic species were measured in TE samples using SPE coupled with GC-MS to provide information on TE composition. The most frequently detected organic compounds included 2-nitrophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 3-nitroaniline, 4-chloro-3-methylphenol, acenaphthylene, benzyl butyl phthalate, bis(2-chloroethoxy)methane, di-*n*-butyl phthalate, di-*n*-octyl phthalate, dimethyl phthalate, diphenylamine, fluorene, Isophorone and pyrene. These compounds were modelled against AER, wet chemistry and sensor measurements to determine whether these compounds could be utilised as surrogates for TE composition and quality.

Table 38 summarises the significant correlations between quantified organic compounds and TE sensor and wet chemistry parameters.

Table 38 Statistically significant linear correlations for specific compounds with TE monitoring parameters

Compound	Parameter	Adjusted R^2	*p*-value
2-nitrophenol	280 nm	0.430	4.60E-02
2-nitrophenol	COD	0.443	3.01E-02
2-nitrophenol	Phosphate	0.472	2.46E-02
2-nitrophenol	TOC	0.586	1.64E-02
2,4,5-trichlorophenol	360 nm	0.671	7.87E-03
2,4,5-trichlorophenol	COD	0.662	4.69E-03
2,4,5-trichlorophenol	Nitrite	0.776	2.39E-03
2,4,5-trichlorophenol	Phosphate	0.926	2.06E-05
2,4,5-trichlorophenol	TOC	0.630	1.14E-02
3-nitroaniline	500 nm	0.449	4.13E-02
3-nitroaniline	600 nm	0.776	2.39E-03
3-nitroaniline	TN	0.599	2.51E-02
4-chloro-3-methylphenol	Chloride	0.753	1.50E-03
4-chloro-3-methylphenol	Conductivity	0.803	1.60E-03
4-chloro-3-methylphenol	Turbidity	0.458	3.91E-02
Benzyl butyl phthalate	500	0.542	2.25E-02
Benzyl butyl phthalate	600	0.846	7.52E-04
Benzyl butyl phthalate	TN	0.671	1.50E-02
Benzyl butyl phthalate	TP	0.558	2.01E-02
Bis(2-chloroethoxy)methane	254 nm	0.708	5.46E-03
Bis(2-chloroethoxy)methane	280 nm	0.670	7.95E-03
Bis(2-chloroethoxy)methane	Chloride	0.458	2.70E-02
Bis(2-chloroethoxy)methane	Conductivity	0.641	1.04E-02
Bis(2-chloroethoxy)methane	Turbidity	0.787	2.06E-03
Di-*n*-butyl phthalate	254 nm	0.560	1.98E-02
Di-*n*-butyl phthalate	280 nm	0.511	2.78E-02
Di-*n*-butyl phthalate	Chloride	0.577	1.07E-02
Di-*n*-butyl phthalate	Conductivity	0.791	1.94E-03
Di-*n*-butyl phthalate	Turbidity	0.473	3.56E-02
Di-*n*-octyl phthalate	Ammonia	0.775	5.53E-03
Dimethyl phthalate	360 nm	0.794	1.85E-03
Dimethyl phthalate	COD	0.903	5.33E-05
Dimethyl phthalate	Nitrite	0.969	6.12E-06
Dimethyl phthalate	Phosphate	0.932	1.53E-05
Dimethyl phthalate	TOC	0.888	2.88E-04
Pyrene	280 nm	0.441	4.32E-02
Pyrene	Ammonia	0.830	2.70E-03
Pyrene	Turbidity	0.432	4.55E-02

Long term TE parameter variation

The potential for sensor data to inform TE parameter variation was achieved using linear modelling and correlation analysis. Long term analytical results on TE parameters were obtained for a selection of sites taking part in the research project. Trend analysis was performed on data from these sites to determine if there were useful correlations between TE parameters.
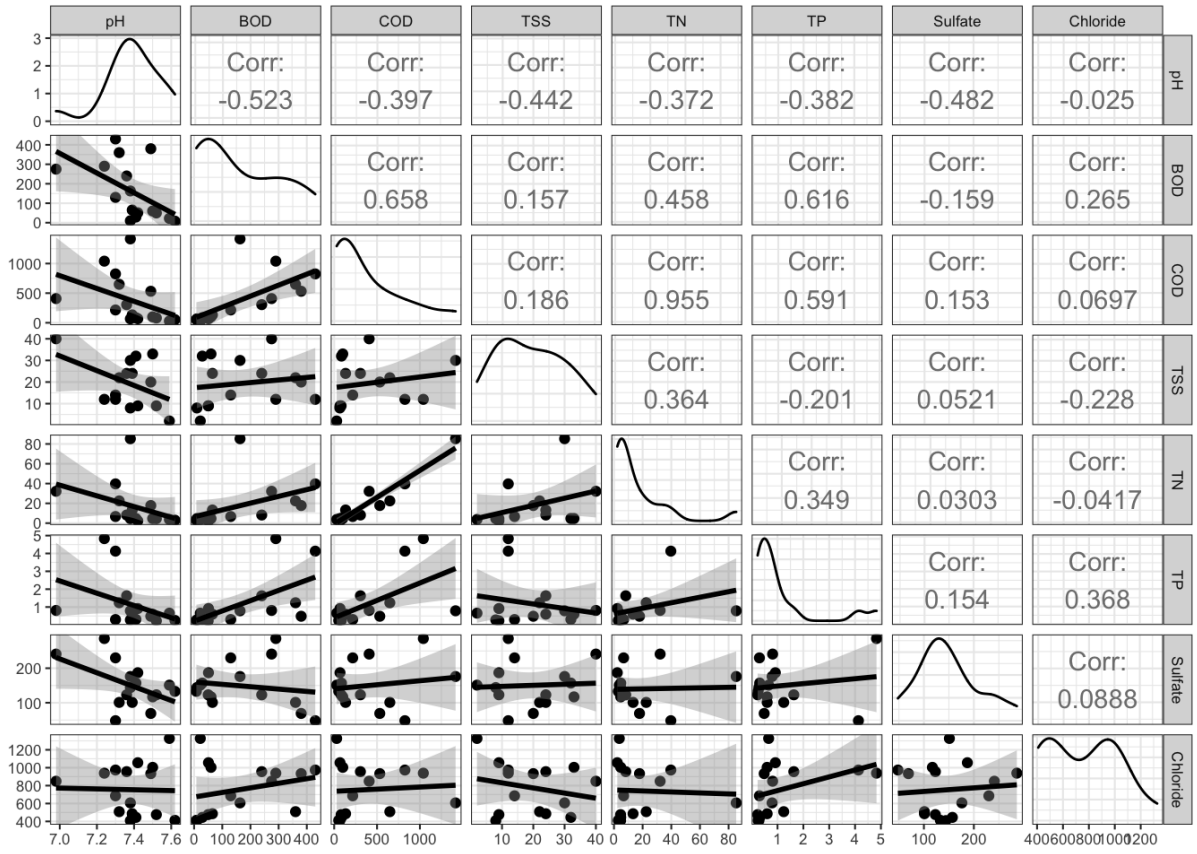
Figure 62 Summary of correlations between TE parameters measured at biopharmaceutical site A

Site A indicated correlations between COD and BOD, as well as COD and TN (Figure 62). This suggested that a surrogate that was linked with COD could be a useful for indicating increased levels of BOD and TN simultaneously. The BOD test is the slowest test to complete due to a necessary holding time of at least 5 days to complete the test. The TN and COD tests require 2 to 3 h to complete, therefore sensor data that provides insight into COD-TN concentrations would provide a valuable surrogate for these three important TE parameters simultaneously.
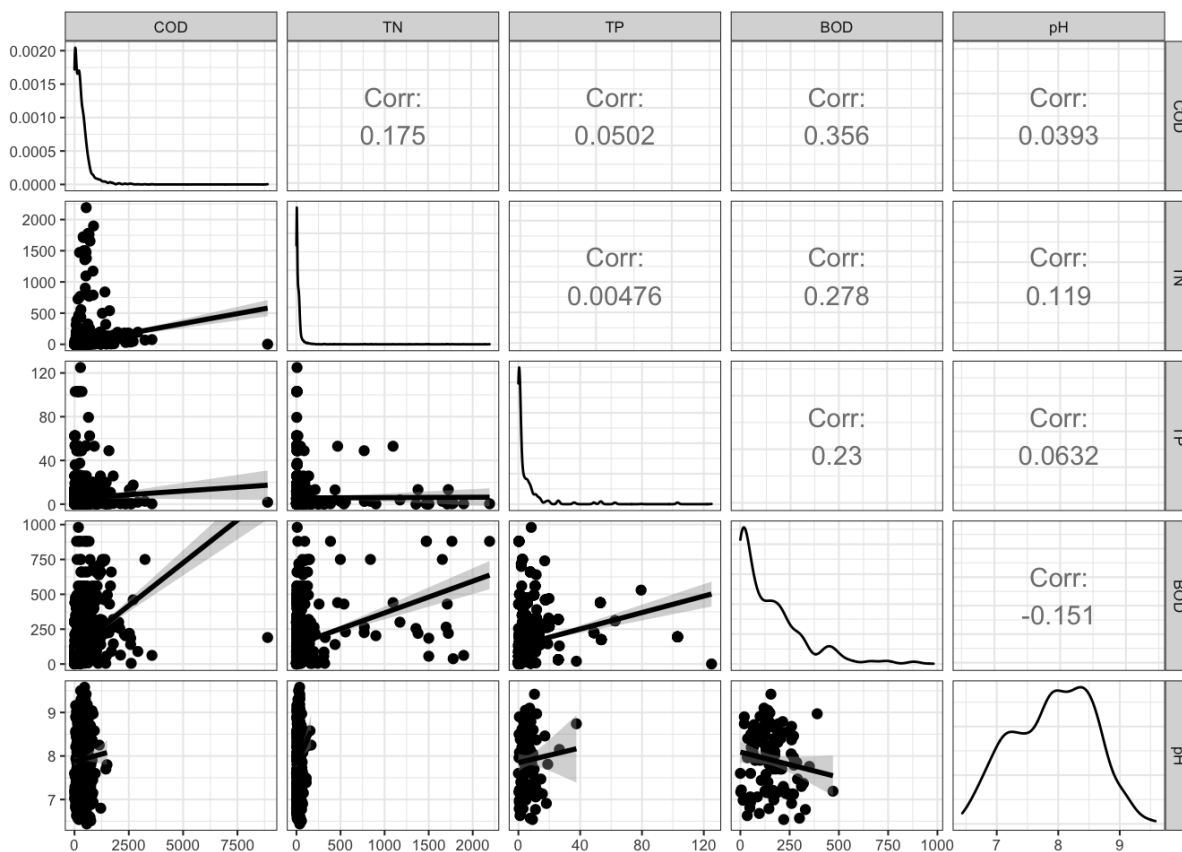
Figure 63 Summary of correlations between TE parameters measured at biopharmaceutical site B

No significant correlations were detected between TE parameters at biopharmaceutical site B (Figure 63). In contrast to site A, site B's COD, BOD, pH, TN and TP all varied independently which suggested that production is more variable at Site B and that each parameter needs to be monitored individually, either using chemical assays or a selective chemical sensors to provide appropriate data on TE composition. Site A and B both produce protein-based pharmaceutical drugs, highlighting large variability between the TE profiles generated by biopharmaceutical companies.
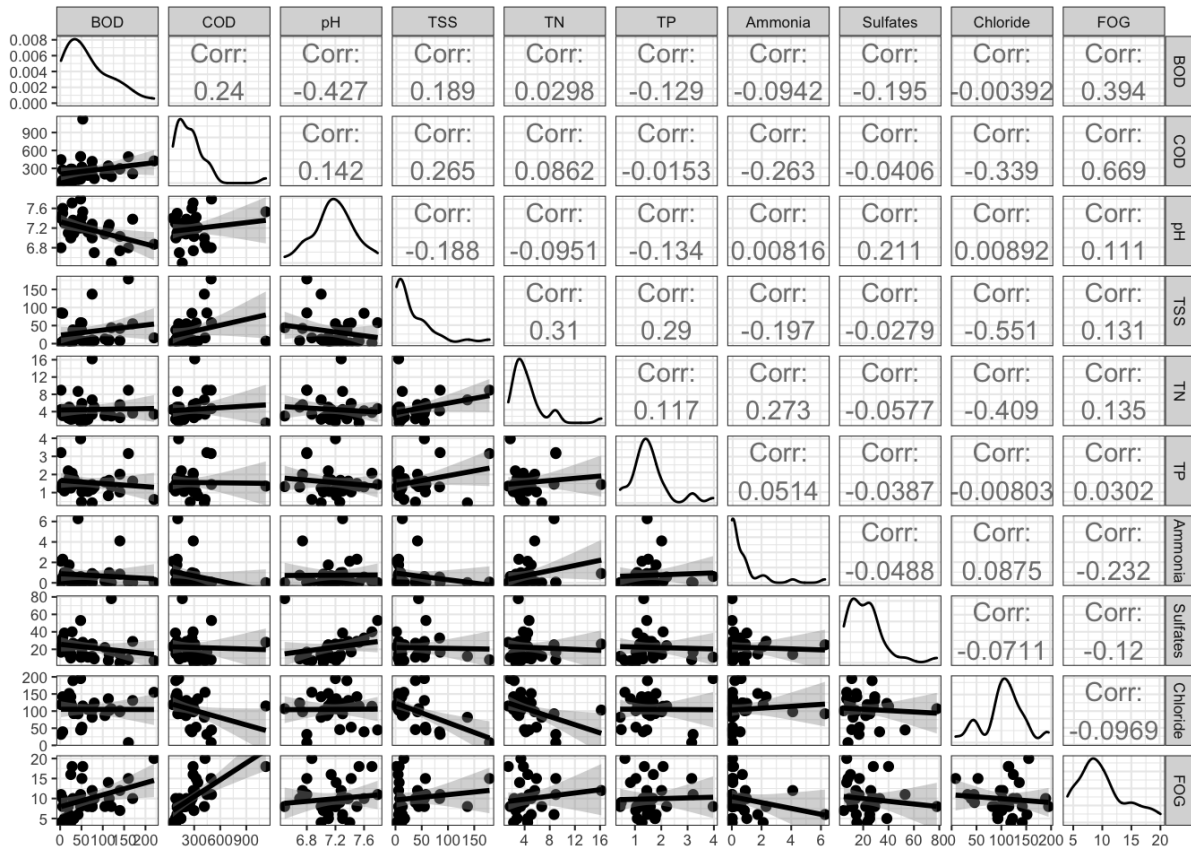
Figure 64 Summary of correlations between TE parameters measured at biopharmaceutical site C (Fats Oils and Greases =FOG)

Site C, in contrast to A and B, produces a portfolio of small molecule pharmaceuticals instead of biopharmaceuticals. Site C showed evidence for linear relations between FOG-BOD and FOG-COD levels and there were also weak correlations between TSS-TN, TSS-TP and COD-BOD. The inconsistencies in correlations between parameters at each of the TE sites within the biopharmachem group highlights that it is not possible to generalise the results of one biopharmachem site to another. This means that sensors or monitoring technologies used must be calibrated based on the properties of each deployment site.
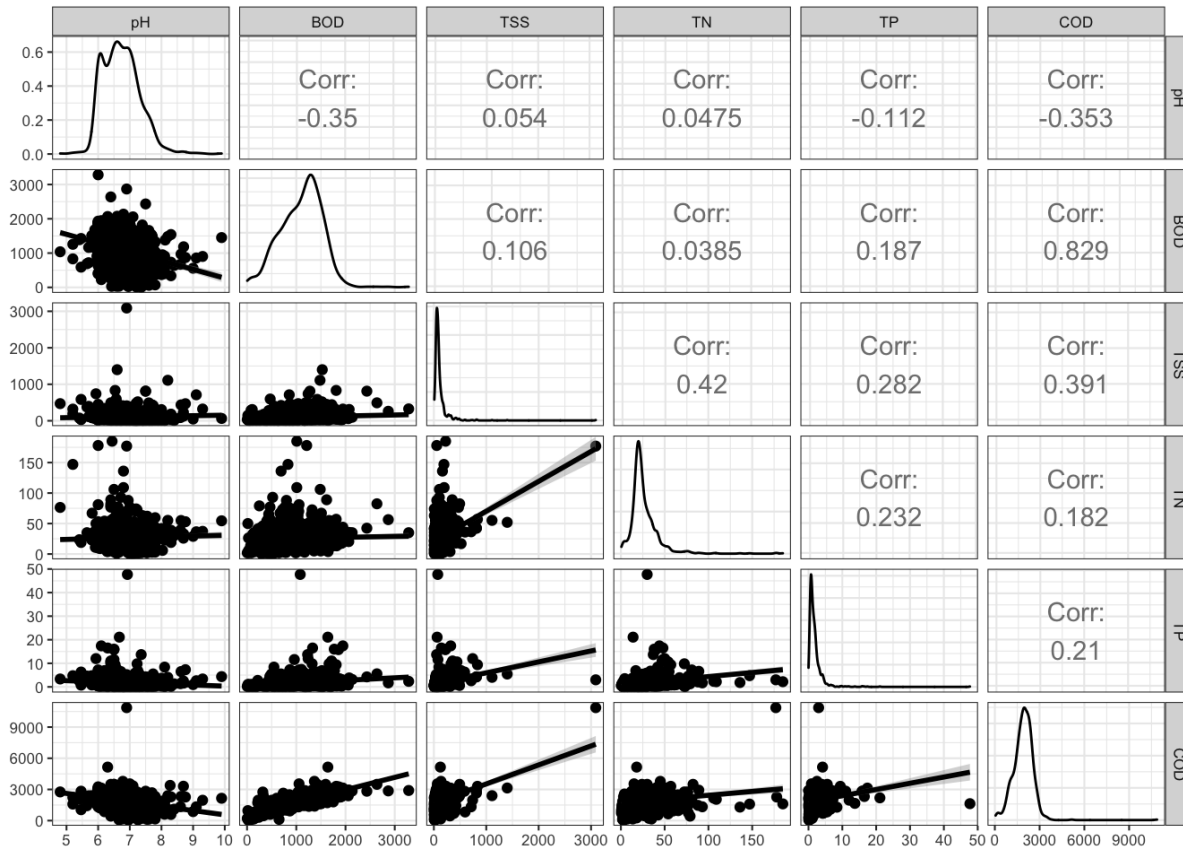
Figure 65 Summary of correlations between TE parameters measured at food/beverage site A

Analysis of TE parameter data from food/beverage site A indicated that COD was correlated with BOD although the prediction bounds of the linear relation are wide and subject to significant variation. Similar to the biopharmachem sector, the diverse portfolio of products prepared by this site contributed to the large variation in TE parameters that results in a lack of strong correlations between parameters.
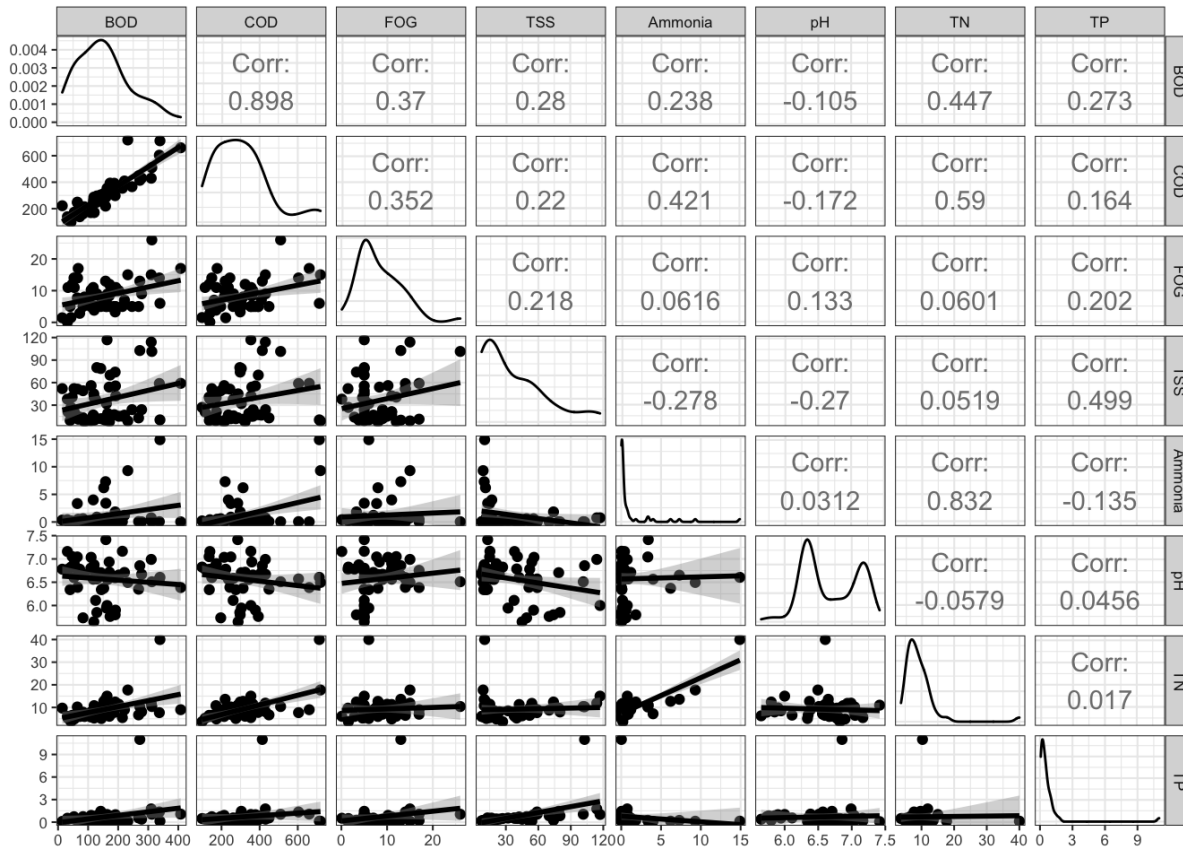
Figure 66 Summary of correlations between TE parameters measured at food/beverage site B

TE parameter data for site B of the food/beverage group revealed a strong linear relation between BOD and COD (0.898) that could be used to inform the levels of either one of these parameters. As previously mentioned the COD assay is much faster than the BOD assay, which is useful for intervening and controlling TE properties prior to release. Additionally the levels of ammonia were well correlated with TN (0.832). This linear relation is valuable as ISE sensor technologies for ammonia provide real-time information on the levels ammonia and TN species. There were also additional weaker correlations between COD and TN, and TSS and TP.
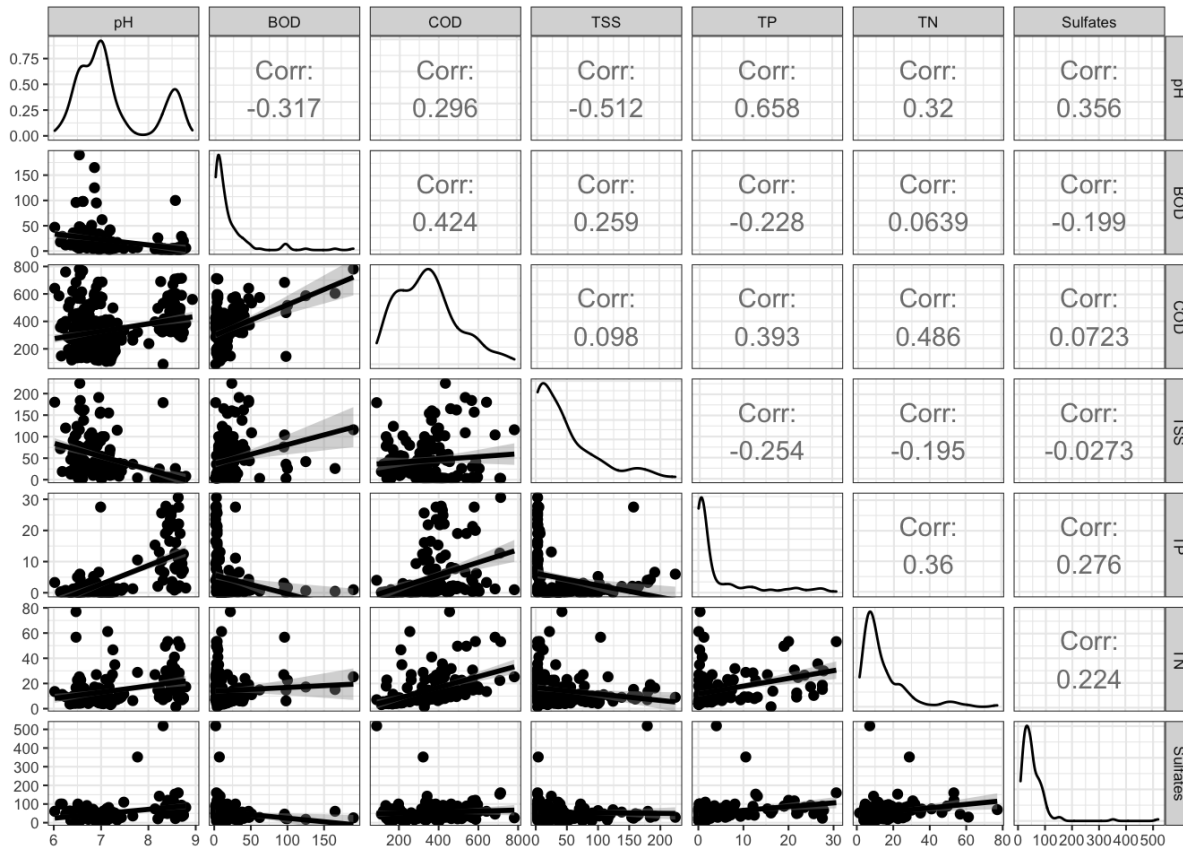
Figure 67 Summary of correlations between TE parameters measured at food/beverage site C

Site C of the food/beverage group showed some interesting pH results with TE pH values averaging to 7 or 8.5 depending on site operations at the time (Figure 67). This is linked the production of different products and changes in pH balancing prior to TE release. COD and BOD were only weakly correlated with each other at this site, and there was a further weak correlation between COD and TN parameters.

Sensor deployment

A sonde platform was deployed at food/beverage Site C to monitor TE emissions over a duration of 20 d. Figure 68 summarises four channels of sensor data collected over the course of the deployment, note that these four channels can be utilised for the calculation of additional parameters such as salinity, TSS and TDS.
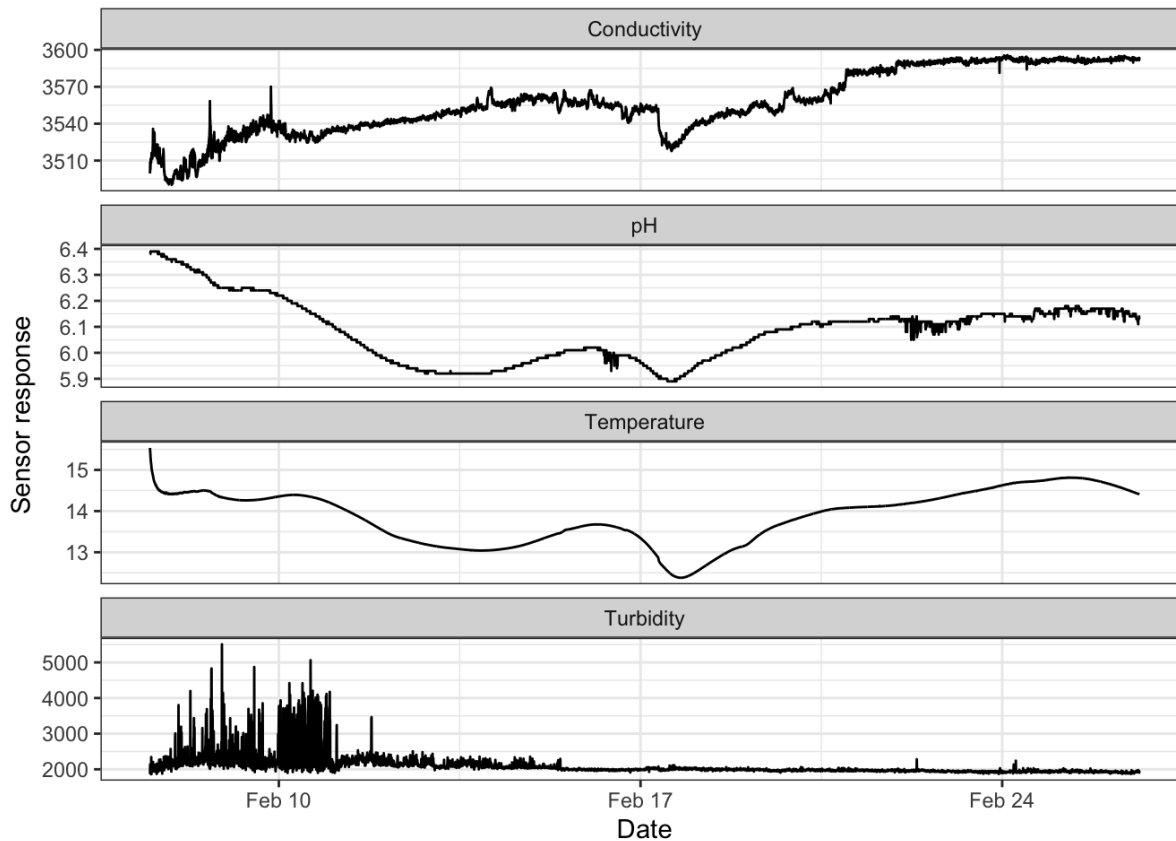
Figure 68 Sensor parameters measured during sonde deployment at food/beverage site C, including specific conductivity (µS/cm), pH (unitless), temperature (°C) and turbidity (NTU)

Site C's TE temperature varied between 12.71 and 14.77 °C and this parameter was used for the temperature correction of pH, conductivity and turbidity measurements as it impacts the acidity, and viscosity of TE which has a direct effect on the other sensor parameters measured. The site's pH varied over a narrow range of 6.37 to 5.92, this is due to pH balancing that is performed on the TE prior to release to sewer. Turbidity measurements indicated substantial variation during the first week of the deployment where there was evidence for higher levels of light scattering species in solution, however the variation decreased and stabilised after the 15th of Feb, which was linked with a change in the production at the industrial site and subsequent modification to TE treatment prior to release. There was no evidence for correlation between pH, nor conductivity measurements. Conductivity was temperature corrected using on-board measurement correction algorithms to account for changes in viscosity as a function of temperature. The conductivity of the TE varied over a narrow range from 3505 to 3592 µS/cm during the deployment.

Daily composite TE samples were collected over the course of the deployment and the parameters pH, COD, TSS, and temperature were measured. Regression modelling was used to determine whether sensor parameters could provide insight into the composition of TE. Real-time

sensor measurements were averaged to daily values to allow comparison with the composite TE samples that were analysed using wet chemistry techniques.
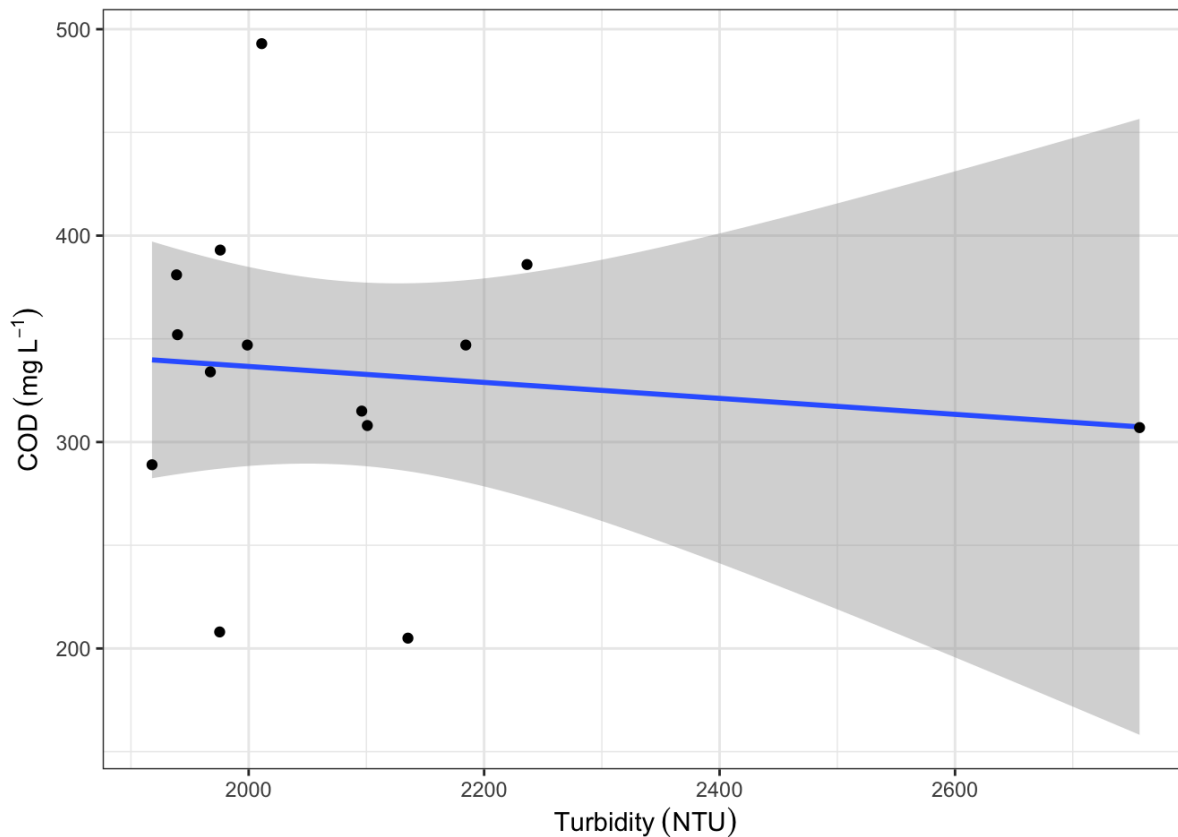
Figure 69 Sonde measured turbidity (daily average) vs COD measurements from daily composite samples at food/beverage site D

COD was found to vary over a range of 205 to 493 mg/L, while turbidity varied over a daily averaged range of 1917 to 2756 NTU. Linear regression between the two parameters is shown in Figure 69, which revealed that there was no significant relationship between the two parameters.
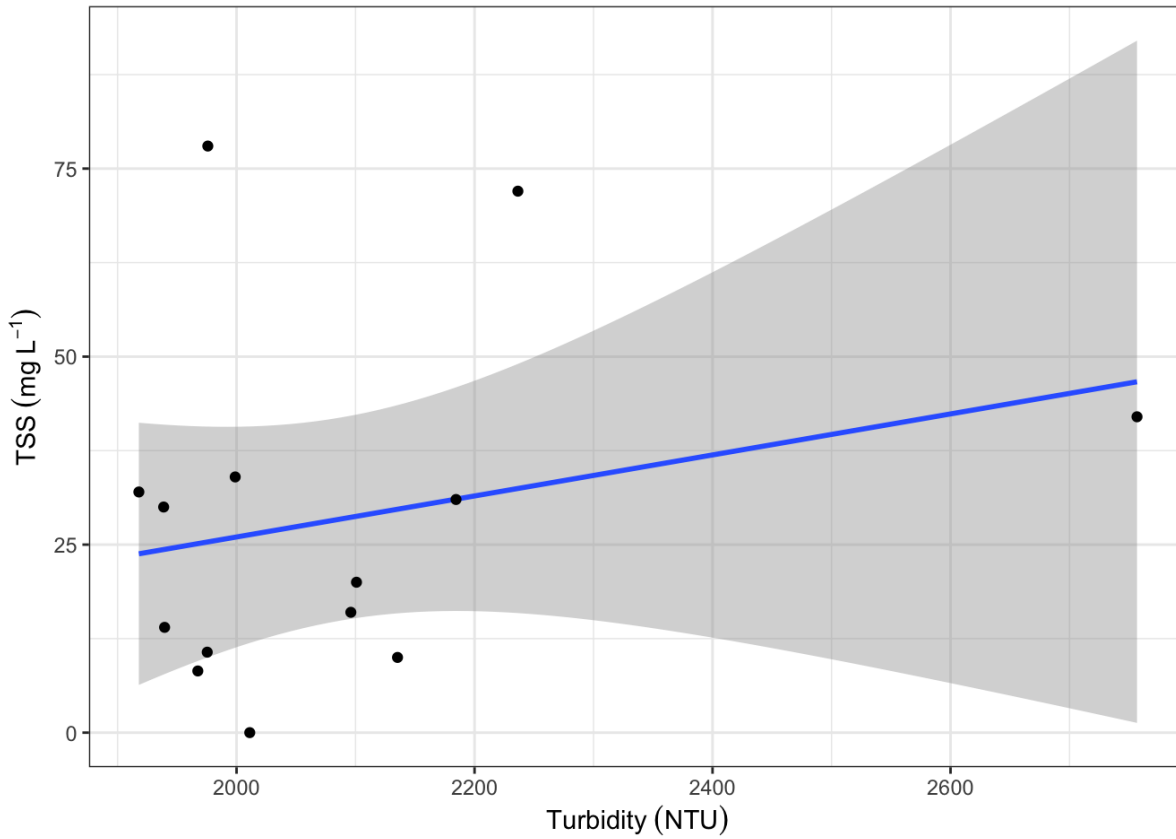
Figure 70 Sonde measured turbidity (daily average) vs TSS measurements from daily composite samples at food/beverage site D

TSS measurements spanned ranges of 0 to 78 mg/L. Linear regression of TSS with turbidity measurements is shown in Figure 70, which revealed that there was no significant linear relationship between the two parameters.
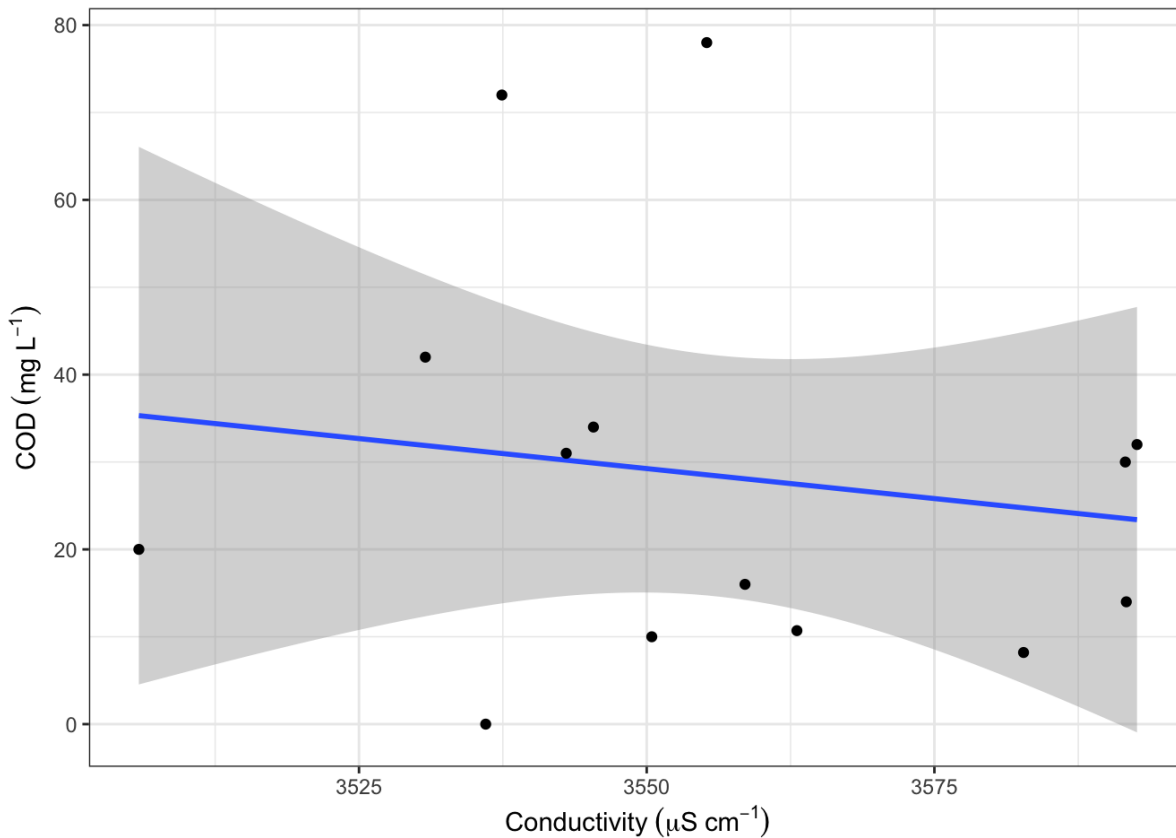
Figure 71 Sonde measured conductivity (daily average) vs COD measurements from daily composite samples at food/beverage site D

Linear regression of averaged daily sonde measurements of conductivity against COD levels indicated that there was no correlation between these two parameters (Figure 71). While the sensor parameters monitored at Site D did not indicate evidence that these sensors could be used to inform TE parameters such as COD or TSS, the correlation and regression analysis performed on sites A, B and C did provide some meaningful information. The operations of site D are highly variable compared to some food/ beverage sites that are focused on more specific products. This variability in production cause significant variation in sensor and TE parameters making it difficult to calibrate sensor values with wet chemistry analysis without more frequent TE sampling.

Conclusions

From the results obtained there is significant evidence for the potential of spectroscopic, conductivity and turbidity sensors for obtaining surrogate information linked to TE parameters. Spectroscopic sensors at UV-vis absorbance's 254 nm and 280 nm were shown to co-vary with COD, TOC and phosphates in TE samples. Measurements of turbidity, pH and turbidity were shown to vary with levels of ammonia, TN, conductivity, and nitrate. Additionally, there is opportunity to leverage commercially available ammonia and nitrate sensors to provide additional

information regarding nitrogen containing species. Finally, turbidity and spectroscopic measurements at 600, 500 and 450 nm were linked with levels of phosphorous and nitrates in TE species. This confirms that commercially available sensors including pH, turbidity, conductivity, and ion selective electrodes (*e.g.* ammonia and nitrate) are able to detect bulk differences in the properties of TE that are relevant to TE quality. Sensors may provide valuable capabilities for obtaining real-time information about the composition of TE, without requiring costly and time consuming wet chemistry based analysis, which could be used to provide information about sewer loadings and potential shock loads downstream to wastewater treatment plants.

The variation in TE parameters and their potential to be monitored using surrogates was assessed for three industrial sectors including the biopharmachem, food/beverage and waste management groups. Nutrient, organic, inorganic and metallic species were correlated with sensor data and compound measurement data using regression and correlations techniques. The present data indicate that the site-to-site variation in TE parameters is highly variable and dependent on the specific operations being carried out at each site. For example, BOD and COD are correlated for some sites, but uncorrelated at other sites. TN and ammonia show promising correlations within the biopharmachem and food/beverage sectors that could be leveraged using ammonia selective electrode technologies. However, sensor and surrogate data need to be individually calibrated and validated for each site of interest to provide reliable information on compound and nutrient levels.

Evaluation of sensor data for the sonde deployment indicated that there were no significant relations between the sonde measured parameters of turbidity, conductivity, pH, TSS, TDS, temperature and monitored nutrient parameters for the site at which the sonde was evaluated. The relatively low variability of the conductivity parameter and high variability of the turbidity parameter meant sensor data did not link with measured TE parameters. Analysis of all-sector TE parameter data suggest that there are moderate correlations between COD-turbidity, ammonia-TN and conductivity-chloride. This initial project shows promise, and future work would benefit from additional sensor deployments. A high volume of continuous sensor data at other sites could confirm if these sensors can provide further insights into real-time monitoring of industrial TE.

6

Project recommendations

Project recommendations

Introduction

This project involved the three main tasks of:

a) Characterising TE from three high risk sectors;

b) Identifying markers or surrogate parameters in TE; and

c) Investigating the applicability of novel sensor technology for monitoring.

The techniques used in the project included wet chemistry, chromatographic analysis and spectroscopic analysis to provide detailed information on the composition of TE derived from three industrial sectors. The methods utilised for monitoring trade effluent are predominantly focused on wet chemical analysis of nutrient parameters of discrete samples. The sample analysis information however is generally only a snapshot of information in a point in time. Therefore, the use of more innovative passive sampling and sensor technologies can provide valuable information for the purposes of determining the properties of trade effluent and strategies in its management once discharge to the public sewer. The results of this research project have highlighted a number of observations in relation to the chemical composition of effluents from the target groups monitored. This information and subsequent sensor evaluations have led to these recommendations.

Recommendations

The data obtained on the composition of TE samples can be used to inform levels of input to sewer systems and the selection of sensor and passive sampler technologies for monitoring TE properties. Furthermore, this comprehensive data set enables the identification of appropriate markers, or surrogate species, for monitoring licensed parameters within TE. The chemical characterisation information identified the levels of commonly monitored species within TE to determine which analytes may be of interest for sensor or passive sampling monitoring. It is recommended that:

a) Where possible, real-time monitoring systems using off-the-shelf sensors should be used to provide temporal trends in effluent composition. This has the benefit of determining if there are any problems with the process or the wastewater management system, as well as highlighting issues with changes in process parameters. It is acknowledged that there is a need for appropriate cost benefit assessments to be carried out to demonstrate viability.

b) Where current sampling approaches are suitable for compliance purposes, additional sampling, passive sampling or long term monitoring can lead to a better management

approach. Real-time data can lead to trend analysis and therefore alerts can be set, to assist in effluent quality management.

c) Suitable passive sampling membranes can provide useful information on effluent quality in relation to certain parameters e.g. nutrient/organics, with a time weighted average at a low cost in comparison to traditional monitoring techniques in the regulation of TE discharges.

d) Where TEs are variable in composition, a real-time system of turbidity or conductivity monitoring should be implemented to ensure early alerts of potential non-compliance.

e) The monitoring burden for companies can be reduced based on a more nuanced approach to sampling based on risk. This can be achieved using passive sampling approaches tailored for certain chemical groups for example nutrients or organic compounds.

Specific sensor suggestions

It was found that testing with **conductivity and turbidity sensors** shows that these commercially available sensors are able to detect bulk differences in the properties of TE samples. This may provide insight into changes in TE composition over time. While conductivity and turbidity measurements have low selectivity for specific targets such as COD or ammonia, knowledge about the composition of specific sectors or sites is important for correlating changes in these sensors with specific monitored parameters. Commercial sensors for **ammonia, nitrite, and nitrate** are available and ammonia sensors are of particular interest due to the variation that this species shows in the biopharmachem, food/beverage and waste management sectors.

Based on the TE parameters measured the **key targets for passive sampling** are recommended to be:

a) Organics such as those derived from COD, TP and TN contributions (both polar and non-polar in nature) and;

b) Inorganics such as nitrates, ammonia, phosphate, iron and aluminium; and

c) Particulates as quantified using TSS and turbidity.

The following **passive sampler phases** and **sensor technologies** are recommended for evaluation due to their capabilities in monitoring the aforementioned parameters:

d) The non-polar octadecyl (C_{18}) Chemcatcher for sampling of non-polar organics;

e) The Hydrophilic-Lipophilic Balance (HLB) Chemcatcher for sampling of polar organics;

f) The anionic Chemcatcher extraction phase for inorganic species; and

g) Turbidity and conductivity sensors.

Future research opportunities

Real time monitoring of TE attempts to move from a reactive control model, to a scheme where the frequency of data collection is rapid enough to allow the prediction and control of TE parameters. However, such real-time monitoring needs to be deployable in a cost effective manner with supporting business cases clearly demonstrating the benefits of such deployment. Thresholds for parameters can be set to enable action to be taken ahead of time to prevent the release of effluent that is no of the desired standard.

a) Sensors are already utilised for the measurement of temperature, pH and flow volumes, however uptake of other sensors has been limited due to the lack of a need to report real-time data or use the data collected. There are a range of sensor technologies including, turbidity, conductivity ion selective electrodes (ISEs), electrochemical and spectrophotometric sensors that are potentially of value to deliver real-time information on TE composition. Further research is required to determine the appropriateness and cost-effectiveness of such sensors in monitoring industrial trade effluent. Results have confirmed correlations between conductivity with chloride levels, TN and ammonia, turbidity and TP, as well as turbidity and COD-TOC. Additionally, links between phosphate-COD-TOC were confirmed. These results suggest that **turbidity, chloride and ammonia sensing electrodes** may be valuable for monitoring these species in real-time.

b) We would recommend **real-time monitoring** of **temperature, turbidity, pH and conductivity** to provide a valuable data tool for monitoring effluent quality. A study should involve a long term deployment of a sonde with these sensors, and parallel water quality analysis to train an algorithm for the particular trade effluent site. This would lead to a real-time monitoring tool that could alert the industry to any water quality issues as they occur.

c) Expanding the analysis to compare **spectroscopic properties** of TE samples with nutrient parameters provided additional capacity for quantifying levels of organic and inorganic species in TE. Further **spectroscopy studies** of effluents would provide a valuable signature of the wastewater and again provide a real-time tool with very rich analytical data to indicate changes in quality as it occurs.

d) Passive sampling (PS) technologies provide a new and selective method of performing composite sampling of targeted species in water, while reducing the need to preserve and transport large volumes of samples. PS devices function by adsorbing dissolved organic, inorganic and metallic species from TE over a deployment duration, thereby providing a composite average of compound loadings emitted by a site. Further research on a series

of trade effluent sites over prolonged periods of time can provide valuable information on water quality as well as time weighted average compositions. In addition, the targeted deployment of PS technologies should be considered to support the ongoing TE risk assessment activities within Irish Water.

7

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Appendix

A Summary of Sensor Deployment Data

TE Site 105

Table 1 Summary statistical data arising from a sensor sonde deployment on-site. Measured parameters include conductivity, depth, ORP, turbidity, pH and temperature. Sampling frequency was set at a measurement every 2 minutes.

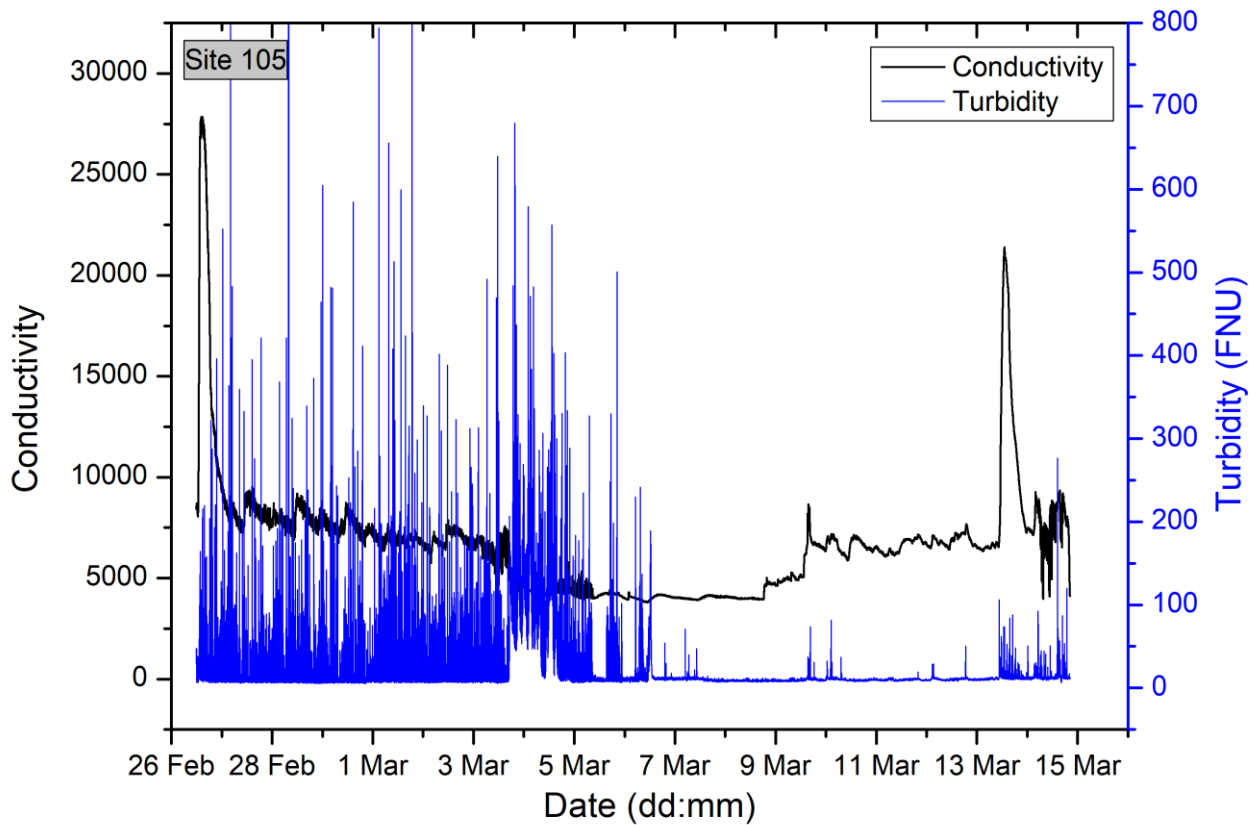|	A	B	C	D	F	G	H
1		N total	Mean	Standard Deviation	Minimum	Median	Maximum
2	Conductivity	12495	6654.85	3002.12	3799.20	6668.00	27859.70
3	Depth	12495	0.16	0.11	-0.17	0.18	0.33
4	ORP	12495	33.30	22.57	-82.20	29.90	136.80
5	Turbidity	12495	25.52	49.71	5.29	10.81	1606.06
6	pH	12495	8.24	0.06	8.13	8.23	8.39
7	Temperature	12495	17.08	0.74	14.83	17.17	19.55

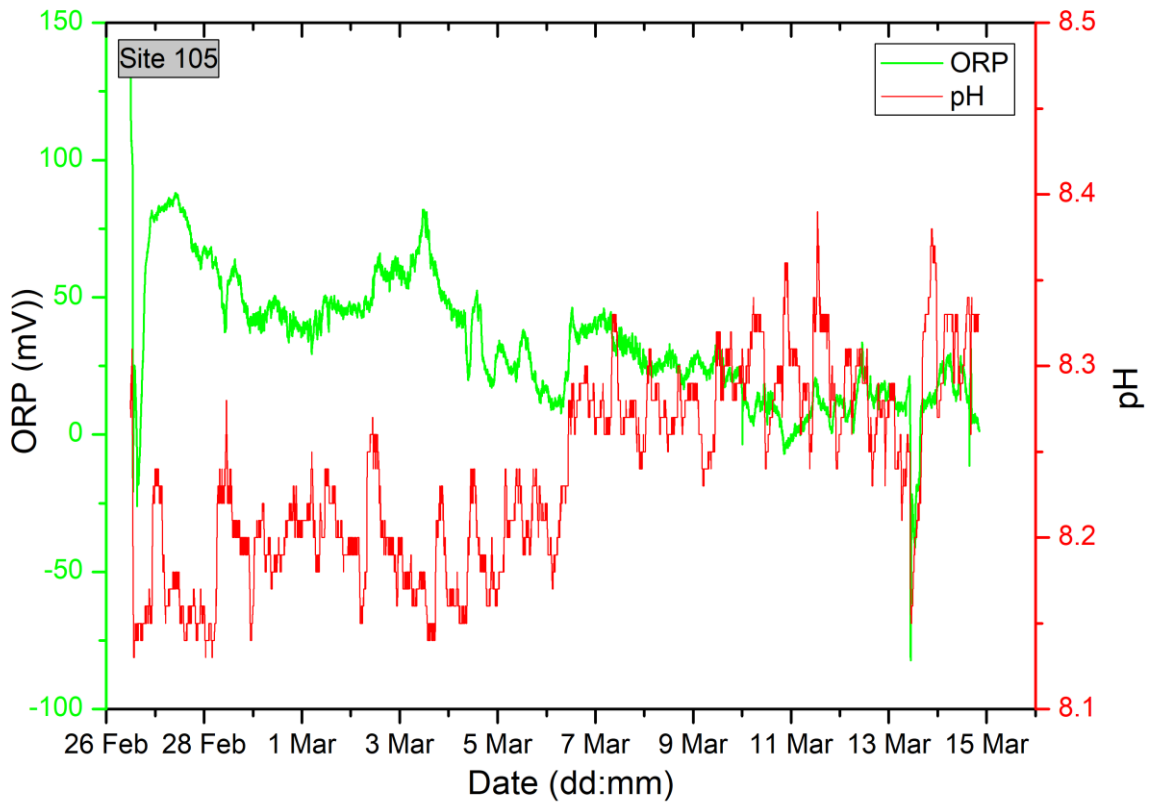**Figure 1: Time series data from the conductivity probe and turbidity sensor at site 105**

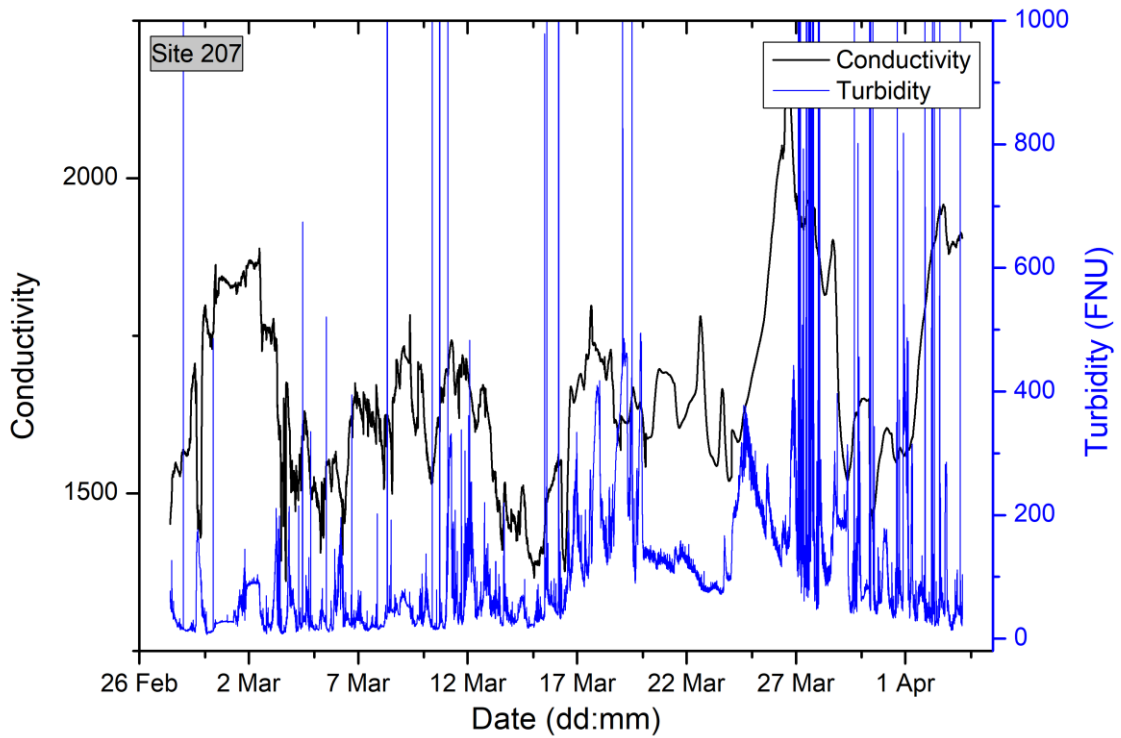**Figure 2: Time series data from the pH and ORP sensor at site 105**

Figure 3: Time series data from conductivity and turbidity sensors at site 207. Sampling frequency is every 5 minutes
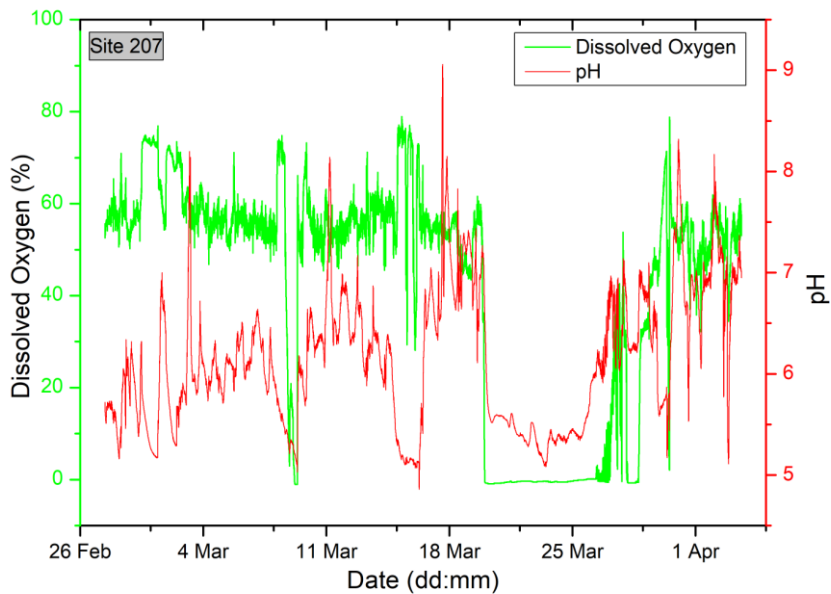

Figure 4: Time series data from pH and dissolved oxygen sensors at site 207. Sampling frequency is every 5 minutes