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Performance of UK wastewater treatment works with respect to trace contaminants

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Abstract

This study examined the performance of 16 wastewater treatment works to provide an overview of trace substance removal in relation to meeting the objectives of the Water Framework Directive (WFD). Collection and analysis of over 2,400 samples including sewage influent, process samples at different stages in the treatment process and final effluent has provided data on the performance of current wastewater treatment processes and made it possible to evaluate the need for improved effluent quality. Results for over forty substances including metals, industrial chemicals and pharmaceuticals are reported. Data for sanitary parameters are also provided. A wide range of removal efficiencies was observed. Removal was not clearly related to the generic process type, indicating that other operational factors tend to be important. Nonetheless, removals for many substances of current concern were high. Despite this, current proposals for stringent water quality standards mean that further improvements in effluent quality are likely to be required.

Key words – priority substance, regulation, wastewater, effluent, trace chemicals

1. Introduction

1.1. *Legislative context and the Chemicals Investigation Programme (CIP)*

Legislation in the field of water and the environment, and in particular in the European context the Water Framework Directive (WFD – EC, 2000), is extending the scope of pollution control measures required to protect surface waters. Environmental Quality Standards (EQSs – EC 2008) - concentration limits that are used to define satisfactory water quality have been established for more than 30 substances that hitherto have not been subject to detailed monitoring or control. In addition, individual national regulators have been required to set their own standards for a further group of potential pollutants. The combined effect of this legislation is to place increasing emphasis on pollution control measures. In order to respond to these new obligations, a clearer understanding is required of the effectiveness of wastewater treatment (WwTW) processes in removing the substances of interest from effluent discharges. To address this issue, UK Water Industry Research (UKWIR) has collaborated with the water industry, the Environment Agency and other UK regulators in the design of

a £25 million programme of investigations (The Chemicals Investigation Programme or CIP) into the management and control of a range of substances that may be present in wastewater treatment works discharges. The overall basis of the programme and the results of effluent monitoring have been described by Gardner *et al.* (2012). This paper reports the outputs of the CIP that relate to the assessment of treatment works performance with respect to a wide range of trace contaminants.

1.1 Fate of pollutants in wastewater treatment

The fate of organic compounds during water treatment is determined by a combination of their physico-chemical properties and the treatment operation parameters and design of the process (Byrns, 2001). Synthetic compounds are removed from waste streams during wastewater treatment either by biological or chemical degradation, sorption to the solid phase or volatilisation (Meakins *et al.*, 1994), (Langford *et al.*, 2005). Biodegradation of some organic compounds occurs when microorganisms use these compounds as carbon source for their growth, although in some cases the microorganisms also transform the compound while using another carbon source (co-metabolism) (Vader *et al.*, 2000). Joss *et al.* (2006) proposed a model for the biodegradation of pharmaceuticals in wastewater treatment, in which he classified the substances according to their degradation constant (k_{biol}). Thus pharmaceuticals with $k_{biol} > 10 \text{ l/g}_{ss}/\text{d}$ (where g_{ss} relates to the suspended solids in the activated sludge plant) are biodegraded to an extent $>$ than 90%, those with $0.1 \text{ l/g}_{ss} < k_{biol} < 10 \text{ l/g}_{ss}/\text{d}$ are degraded in some extent and finally those with $k_{biol} < 0.1 \text{ l/g}_{ss}/\text{d}$ are persistent and remain in wastewater. However, it is acknowledged that sludge characteristics also play a role in the removal rate. The octanol water partition coefficient (K_{ow}) is an indicator of the hydrophobicity of organic compounds and its value determines the behaviour of pollutants along the process; therefore, those hydrophobic chemicals which have not been settled and removed with the primary sludge, reach the secondary treatment associated with the particulate matter, whilst the most hydrophilic and soluble ones remain dissolved. According to the model developed by Byrns (2001), chemicals with $\log K_{ow}$ between 1.5 and 4 are biodegraded, whilst more hydrophobic substances ($\log K_{ow} \geq 4$) are mostly adsorbed into the sludge and the most soluble ones ($\log K_{ow} \leq 1.5$) tend to remain dissolved. However, it has also been suggested that partition to solids has to be taken into account for $\log K_{ow} \geq 3$ (Teske and Arnold, 2008). Nevertheless, sorption to solid matter cannot be accounted for solely by hydrophobicity. Other physicochemical processes, including ionic interactions with charged solid surfaces, can play a part. In general, pharmaceuticals are not likely to adsorb to sludge and their removal mostly occurs as a result of degradation (Radenović *et al.*, 2009; Ternes *et al.*, 2004). Parameters other than $\log K_{ow}$, such as the ratio between the concentrations of a substance in the solid and in the aqueous phase at equilibrium conditions ($\log K_d$), have been proposed (Ternes *et al.*, 2004; Carballa *et al.*, 2005). Biodegradation in secondary treatment is also influenced by factors that affect bacterial growth such dissolved oxygen, temperature and pH (Gomes *et al.*, 2011).

It is generally accepted that suspended-growth biological processes such as activated sludge (AS) are more efficient than fixed-film processes (trickling filters) in the removal of chemicals from wastewater and some research corroborating this have been completed, both concerning

pharmaceuticals and illicit drugs (Jones *et al.*, 2005; Bartelt-Hunt *et al.*, 2009; Falås *et al.*, 2012) and natural and xenoestrogens (Teske and Arnold, 2008). However, only a few studies compare quantitatively the performance of these two different processes. Camacho-Muñoz *et al.* (2011) reported that conventional treatment (in which they include AS) was more efficient than low cost ones (in which they included TF), with an overall removal rate of 64% and 55%, respectively – but no uncertainty around these figures were provided. However, Miège *et al.* (2009) compiled data from previous scientific publications to assess the removal efficiency of pharmaceuticals and personal care products in WwTWs, and they found attached growth processes (including TF and biodiscs) to be more efficient than AS in removing estrone, 17- α -estradiol, 17- β -estradiol and sulfamethoxazole.

The removal of metals in wastewater treatment is reported to be highly variable (Chipasa, 2003; Da Silva Oliveira *et al.* 2007). However, the mechanisms of removal are thought to be similar in the two main process types; a few publications found in the literature support the opinion that TF is less effective than AS (Ziolko *et al.* 2009; Santos *et al.*, 2010). It has been suggested that this difference is due to the superiority of activated sludge in removing suspended solids, which also leads to removal of insoluble metals (Crane *et al.*, 2010).

This study examined the performance of 16 WwTWs to provide a national overview of trace substance removal in relation to meeting the objectives of the Water Framework Directive (WFD). It was intended that outcomes from this programme would: (1) inform on the performance of WwTWs in general and their individual unit treatment processes; and (2) provide guidance on options available to improve effluent quality.

2. Materials and Methods

1.2. Selection of WwTWs

The 16 WwTWs selected represent a cross-section of works types currently in operation in the UK and include activated sludge plants (ASPs), trickling filters, membrane bioreactors (MBRs) and oxidation ditches (OD). These works were a subset of the larger set of 160 works that had been selected for the previous effluent quality study (Gardner *et al.*, 2012) as representative of UK WwTWs. Table 1 provides a summary of works process types and consented flows, which ranged from 740 – 72,000 m³/d . The population equivalents for these works ranged from 3,424 – 205,935 which was representative of the size profile of works present in the UK serving over 70% of the national population (Gardner *et al.*, 2012).

The total number of samples taken at any given WwTWs was approximately 150. Therefore, over the 16 WwTWs, approximately 2,400 samples were taken, involving over 150,000 determinations. Spot samples were collected throughout the works to include influent, settled sewage, final effluent and sludge. Where tertiary treatment was present, an additional sample was taken post the secondary stage (secondary sewage). All works were sampled on a monthly basis for a one-year period,

throughout 2010/2011. To assess within-day variability, a minimum of two samples were taken from each site over a 12-hour period (08.00h – 20.00h). At least one sludge process sample was taken on each visit; sludge sampling varied depending on the types of process employed at each works and accessibility issues (Table 1). The analytical methods and performance targets for the 64 trace determinands and sanitary determinands this study has considered were reported in Gardner *et al.* (2012)

1.3. *Data handling and statistical analysis*

Data processing involved taking the average concentration for each sampling day. Mean, median and percentiles were calculated from the daily average values for each WwTWs and determinand. Fractional removal data were calculated from overall median values at each process stage and across the whole works.

Prior to principle components analysis (PCA), the dataset was reviewed in order to ensure suitability for assessment using this technique. Initially, compounds with a high proportion of 'less than' (not detected) values were excluded, and subsequently, bivariate correlation between chemicals was also checked (Sharma, 1996). To assess the correlation between variables, both Pearson and Spearman correlation factors were used since some of the variables were not normally distributed. One of the variables in each correlated pair with a correlation factor > 0.9 (Field, 2009) was excluded in order to create a dataset without redundant variables. The number of variables (chemicals) included in the PCA analysis was then reduced, as the number of sites in relations to variables resulted in a non-positive definite correlation matrix (Field, 2009). At this point, the criterion for inclusion was based on compounds identified as of interest at a national scale in the UK (Gardner *et al.*, 2012). The statistical analyses were performed with *PASW Statistics 18* (free from SPSS) and *Scout, 2008* (free from the US EPA).

3. Results

This paper presents the data collectively for all 16 works examining influent concentration variation and trace chemical removals through primary, secondary and tertiary processes. The objective is to focus on general works performance especially in relation to comparisons over secondary treatment processes rather specific features of individual works.

There was a good comparability of data for occurrence of chemicals in wastewater effluents between the national effluent programme (Gardner *et al* 2012) and this study is demonstrated in Figure S1.

3.1 *Influent concentration variations for sanitary parameters and trace chemicals*

Table 2 provides a statistical summary of wastewater influent concentrations from all of the 16 WwTWs. This represents at least 28 - 30 crude wastewater influent samples per works over a 12 month period. The general characteristics of the influents in relation to sanitary parameters indicated

that they were representative of municipal wastewater from a combined sewer network with industrial inputs constituting <20% of the flow. Overall, no variation in relation to season or temperature was observed for the sanitary parameters or the trace substances which are discussed in more detail below.

The concentrations of the trace substances in the influent were all above limits of detection and were detected throughout the UK. The metals, aluminium and iron had the highest overall detected mean values of 1,722 and 2,483 µg/L respectively, with just 3% and 10% in the dissolved phase (Table 2). Total zinc concentrations (180 µg/L) were an order of magnitude lower, though a higher proportion (23%) was dissolved. The between-works coefficient of variation (CoV) for metals was in general higher than for the sanitary parameters, however, total zinc had the lowest CoV (0.4) indicating consistent occurrence throughout the United Kingdom. Both copper and nickel were also observed to occur in the dissolved phase, at 30% and 65% respectively; this may have implications for their removal during treatment. Lead was predominantly associated with solids, and would be expected to be removed during primary sedimentation.

In relation to the “regulated and emerging organic chemicals”, the most abundant chemicals were ethylenediaminetetraacetic acid (EDTA - 585 µg/L) followed by the plasticisers diethylhexylphthalate (17.8 µg/L) and bisphenol-A (2.05 µg/L). Variability in bisphenol-A concentrations in particular was high. Further substances occurring at concentrations > 1 µg/L were nonylphenol, triclosan, naphthalene and 2-amino-3-(3-hydroxy-5-methyl-isoxazol-4-yl)propanoic acid (AMPA). The widespread use of triclosan across the United Kingdom was reflected in a low CoV (0.23) - equivalent to those of the sanitary parameters. The polycyclic aromatic hydrocarbons (PAHs) were detected between 0.03 – 0.13 µg/L. The lowest concentrations reported reliably as greater than limit of detection were for the bromodiphenyl ethers (BDEs - congeners 47 and 99) and tributyltin (0.005 µg/L). The BDEs had a low CoV, whilst tributyltin was of a higher CoV possibly reflecting disparate, point sources.

Pharmaceuticals were detected in all influent samples, reflecting their widespread use. In particular, concentrations of over the counter drugs such as ibuprofen and diclofenac averaged 18 µg/L and 1.7 µg/L respectively. The antibiotics (erythromycin, ofloxacin and oxytetracycline) were also widely observed with mean concentrations ranging from 0.18 – 3.6 µg/L. Similarly the natural steroid estrogens, together with the synthetic hormone 17α-ethinylestradiol, were ubiquitous although at lower mean concentrations ranging from 0.001-0.049 µg/L with small CoV values.

3.2 Assessment of chemical removal through wastewater treatment processes

Overall, the fractional removal of solids (total suspended solids [TSS]) and bulk organics (biochemical oxygen demand [BOD]) was high (>0.87 for TSS and >0.94 for BOD; Figure 1) in all works, with final effluent consistently achieving consent levels (Table 1). Ammonia removal ranged from 0.03 in a

carbonaceous OD to 1 in fully nitrifying works. In the seven works with a phosphate consent (Table 1) the fractional removal was >0.68 which was higher than the non-phosphorus consented works.

In relation to overall total metal removal, poor fractional removals (0.25; Figure 1) were observed for nickel, which is a soluble metal (65% detected in the dissolved phase). In contrast, the highest removals were observed for less soluble metals, aluminium and lead, with overall fractional removals of 0.96 and 0.9 respectively. Dissolved zinc, mercury, reactive aluminium and nickel were not readily removed (<0.5 fractional removal) with concentrations of dissolved nickel increasing through the works (Figure 1). The regulated and emerging chemicals appear to form two groups, in relation to removal across the works. The water-soluble regulated and emerging chemicals, such as EDTA, glyphosate and mecoprop, exhibited poor fractional removal (0.3 – 0.45). Some of the PAHs (anthracene, fluoranthene, naphthalene, benzo(b)fluoranthene and benzo(k)fluoranthene) were also poorly removed (0.25 – 0.6). In contrast, more efficient removals (>0.8) were observed for the plasticisers bisphenol A and diethylhexylphthalate, the flame retardants (BDEs 47, 99), nonylphenol, tributyltin, triclosan, bentazone and the higher molecular weight PAHs (benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene) (Figure 1). The pharmaceuticals again showed a wide spectrum of removals ranging from 0.21-0.99, following the order: ibuprofen > salicylic acid > oestradiol (E2) > oxytetracycline > oestrone (E1) > 17-alpha-ethinylestradiol (EE2) > ofloxacin > erythromycin > fluoxetine > diclofenac > propranolol.

The removal of trace chemicals and sanitary parameters over primary treatment is shown in Figure 2. Effective removal of TSS (0.58) was observed with a reduction in bulk organics of c. 0.3. As anticipated, dissolved metals were poorly removed during primary treatment in comparison with total metals. Overall, Figure 2 demonstrates that the more hydrophobic chemicals such as PAHs and flame retardants were more effectively removed than soluble chemicals such as EDTA, mecoprop, E1 and glyphosate. Nevertheless, comparison with Figure 1 clearly shows that although some removal occurs during primary sedimentation there must be further fractional removals of chemicals in the secondary or subsequent treatment processes to achieve fractional removals of >0.6. This is also highlighted in Figure 3 which shows the sequential removal through the treatment for a selected range of trace chemicals and sanitary parameters.

The reduction of TSS, BOD and chemical oxygen demand (COD) was observed in primary sedimentation (Figure 3). Correspondingly, removal of most (though not all) chemicals also occurred in primary sedimentation (Figure 3). Removal in primary sedimentation was observed to be enhanced in works where iron dosing prior to the primary treatment process occurred (Figure S2). This 'heat map' of fractional removals for works 2 and 4 clearly shows the effect of iron dosing on the removal of trace chemicals associated with solids, although no enhancement of removal for the more water soluble chemicals (e.g. EDTA, mecoprop, E1 and glyphosate) was observed. However, not all substances were removed during primary sedimentation; the steroid estrogens (E1 and EE2) were

seen to increase in concentration, probably as a result of deconjugation and biotransformation (Figure 3).

Following primary treatment, variable removal of trace chemicals was observed in the biological secondary treatment processes. The dissolved metals copper and zinc exhibited different behaviours with copper being removed - reflecting its affinity for organic material (Figure 3). In the same manner, hydrophobic substances, such as the flame retardants and PAHs were effectively removed with fractional removals of up to 0.95 observed (Figure 3). In addition, some of the pharmaceuticals (ibuprofen and oxytetracycline) and the natural steroids E1 and E2 (Figures 3) are also well removed during secondary treatment. However, a number of other pharmaceuticals are not substantially reduced in concentration in secondary treatment. Notable amongst these are propranolol, diclofenac and EE2 (Figures 3).

Further investigation of the biological processes indicates differences between the process types included in the study. The heat map of fractional removals achieved across the biological process (Figure S2) clearly demonstrates that higher fractional removals (>0.9) occur more frequently in ASPs and MBR works. However, it is important to note that TF, far from being ineffective, can also achieve high removals of some substances such as bisphenol A, ibuprofen, salicylic acid and E2 (Figure S2). Indeed there is a range of performances for organics with some trickling filter works performing well in terms of removal and achieving equivalent removal to ASPs (Figure S2). The results of the PCA are shown in Figure 4. A plot of 14 of the works by type (ASP, TF and MBR) against the first and second principal components shows overlap of process types along principal component 1 (PC1; the x axis). The variables that influence the position along the x axis are trace substances with a high loading on PC1 (Table 3). These are predominantly organic chemicals (ibuprofen, triclosan, E2 and BDE47) along with copper, the removal of which is influenced by organic materials. There is a clearer separation of ASP and TF works along PC2 (the y axis), the variance of which is strongly influenced by total zinc, tributyltin, E2 and total copper.

Although there are differences between the biological process types, albeit with overlap, between TF and ASP, it was apparent that differences in overall removal were less pronounced when the performance was assessed through the entire works (primary through to effluent). In Figure 5 the influent concentration was plotted against the final effluent concentration to achieve a simultaneous visualisation of relative removal and concentration for different works when influent concentration levels vary. The dotted line is the median influent versus the median effluent. Therefore, works to the left and above this line show better removal than those lower and to the right of the line. In general, for total copper the ASPs are clustered to the left of the line indicating improved performance in comparison to TFs works which are to the right of the line. However, for total zinc four of the TFs appear to outperform most of the other ASPs. In general, for BDE47 and benzo(g,h,i)perylene there was equivalent performance between ASP and TF works. The same performance characteristics were also observed for tributyltin and triclosan (Figure 5). In Figure 5 there is some evidence that for

ibuprofen removal across the whole works is less effective where TFs are used. However, for the other pharmaceuticals, such as propranolol and diclofenac, TF-based works are as (if not more) effective.

Although the biological process is key to trace substance removal efficiencies, it is apparent from Figure 3 that further incremental removal does occur in tertiary treatment processes present in many treatment works to ensure improved effluent quality in terms of TSS or ammonia concentrations. When the removal achieved in TF works overall including tertiary treatment is compared to secondary removal alone, it was apparent from the heat map (Figure S2), that there was a strong shift to green (≥ 0.93) when compared to the removals for the biological processes alone (Figure S2). During wastewater treatment trace chemicals may be removed by biodegradation or adsorption to solids. Therefore, chemicals which are not biodegraded can be retained in the solids.

3.3 Concentrations of trace chemicals in treatment works sludges

The sludge data presented in Table S1 correspond to samples collected from 16 works. All of the sludges analysed were untreated samples, prior to further sludge stabilisation, such as anaerobic digestion or thermal treatment. The sludges analysed were six primary sludge samples, five combined primary and humus returns and two OD sludges. The sludge characteristics are reported in Table S1 and the dry solids concentrations were indicative of untreated sludges. Concentrations for selected substances (ibuprofen, BDE47, propranolol, oxytetracycline) at each works are shown in Figure 6 a-d.

Zinc and copper were observed at the highest concentrations in the sludges with mean concentrations of 493 mg/kg and 239 mg/kg respectively. Cadmium and mercury, as expected from the influent concentrations, were at lower concentrations in the sludge, with a mean of 0.76 mg/kg and 0.70 mg/kg, respectively. The variation in metal concentrations over all the sludge types analysed was approximately one order of magnitude between the minimum and maximum.

The regulated and emerging organic chemicals were observed in all sludge types and all of the 16 works. The DEHP concentrations ranged from 0.63 mg/kg to 84 mg/kg, which could reflect the wide variation in catchment use. In contrast, tributyltin and the BDEs were observed over a narrower range of concentrations, notably 0.01 – 0.05 mg/kg and 0.01 – 0.07 mg/kg respectively. The range of sludge concentrations for the pharmaceuticals was of a similar order of magnitude; for example ibuprofen concentrations ranged from 0.01 – 0.67 mg/kg. Concentrations of oxytetracycline, however, were higher (1.15 – 43 mg/kg) with respect to other pharmaceuticals, due to the different binding behaviour of this substance (e.g. Jelic *et al.*, 2012).

The relative consistency in sludge concentrations across all works for some chemicals is possibly a result of consistent domestic use in catchments, while for other chemicals wider variations may reflect more specific point inputs.

4. Discussion

This study presents a generic national picture of the performance of 16 WwTWs for the removal of trace chemicals. This is complementary to further examples in the literature of studies at specific WwTWs for metals (Ziolko *et al.*, 2009) and organic chemicals (Carballa *et al.*, 2007; McAdam *et al.*, 2011). To achieve removal of chemicals, a number of removal mechanisms occur during wastewater treatment. For metals, which cannot be degraded, removal must be by adsorption to solids, which will result in their presence in sludges. However, for organic chemicals a combination of adsorption and biodegradation is possible.

The present study of 16 WwTWs has highlighted that for metals, removal of the dissolved fraction is the major challenge. Efficiencies in the removal of copper and zinc are related to aspects of metal complexation (Constantino 2012). Copper in particular has a strong affinity for a broad range of dissolved organics whereas wastewater effluents can contain substances that complex other metals such as zinc more strongly than naturally occurring humic substances. At a national scale in the UK zinc is of concern in relation to receiving water quality (Gardner *et al.*, 2012). This study has observed removals of dissolved zinc varying from 0 – 70% in the secondary treatment processes. This broad range is commensurate with other studies 30 – 79 % for example Santos *et al.* (2010). Dissolved copper removals also varied from 38 – 90% in this study equivalent to the 17 - 94% reported during secondary biological treatment at trickling filter works (Ziolko *et al.*, 2009). This further highlights the range of removals that can occur for particular unit treatment processes. Although ASPs have been reported to achieve higher removals (50% for dissolved copper) than TFs, the removal values reported for this process also vary widely. However, data are usually reported for total metals with removal ranging from 25% (Roberts *et al.*, 1977) up to 79% (Ziolko *et al.*, 2011). Therefore, the ultimate performance, as observed in this study, is highly variable and depends on both physico-chemical characteristics of the wastewater (Constantino, 2012) and operational parameters (Ziolko *et al.*, 2009). An understanding of metal behaviour and removal processes has led to the conclusion that reducing TSS and BOD will lead to reduced concentrations of dissolved and total metals in effluents (Ziolko *et al.*, 2011).

The regulated and emerging organic trace substances such as industrial chemicals TBT, triclosan and DEHP, along with the pharmaceuticals, PAHs and BDEs (47, 99), pose an important compliance risk on account of the relatively low EQS that have been set or proposed (Gardner *et al.*, 2012). This is despite high levels of removal achieved during wastewater treatment for some of these chemicals.

It is generally accepted that for organic chemicals removal during wastewater treatment occurs predominantly during the biological treatment process (Suarez *et al.*, 2008). However, removal by adsorption to solids does occur during primary sedimentation and the removal of hydrophobic chemicals during this stage may be enhanced by the use of coagulants. Carballa *et al.*, (2005). Reported that where solids removal at the primary stage was particularly high (80% compared with a

typical 40-50%), the corresponding removal of chemicals was also higher. Tributyltin was observed to be more susceptible to removal at the primary stage than triclosan or DEHP. However, other site-specific studies have demonstrated poor removal of tributyltin during primary treatment (Scrimshaw *et al.*, 2013). The higher molecular weight PAHs, which are also hydrophobic, appeared not to be removed well during the primary treatment stage, indicating that there is no nationally consistent link between hydrophobicity and removal with solids. This point is further emphasised by the fact that BDEs are shown to be removed to a larger degree during biological treatment rather than primary settlement.

At a national scale, during secondary biological treatment, although there were differences in the performance of AS and TF processes for the removal of trace chemicals there was significant overlap between processes, with TF outperforming some AS works. In AS works the removal of trace chemicals is known to be affected by operational and design parameters such as redox conditions (Joss *et al.*, 2005; Svenson *et al.*, 2003) hydraulic retention time (Johnson and Sumpter, 2001), loading rate and solid retention time (Clara *et al.*, 2005, Vader *et al.*, 2000]. Similarly parameters which can affect performance at TF works include wet ratios and filter media surface area. In addition, the introduction of recirculation could improve chemical removal in TF (Yang *et al.*, 2009) with sorption rates of trace chemicals being linked to mass transfer limitations and the type of extracellular polymeric substances (EPS) within the trickling filter biofilm (Writer *et al.*, 2011). However, fixed-film TF processes are not as extensively studied as suspended-growth processes, such as AS. Therefore, at a national level, our study indicates that performance at some works might be optimised to provide incremental improvements in the removal of trace chemicals.

It is also important to remember that undue focus on removal efficiency can tend to obscure the most important considerations relating to likely compliance with the objectives of the WFD. The key metric for wastewater treatment remains effluent quality rather than removal. There are a range of approaches that can be considered as part of a programme of measures to improve wastewater effluent quality. These could include:

- a) Treatment optimisation of existing processes and/or addition of tertiary processes, such as sand filters or reed beds - This could achieve the incremental change required. This would involve understanding the relative performance of the treatment works in relation to that of the best performers in this study and the literature. An example where this might be applied would be in enhancing solids removal and subsequently that of hydrophobic chemicals and optimisation of operational parameters for biological secondary treatment such as contact time. These approaches could be applied for WwTWs achieving a moderate fractional reduction (0.6 – 0.9) for pharmaceuticals, such as fluoxetine, oxytetracycline, as well as E2, E1 and total metals.

New approaches- This includes source control to reduce trace chemical loads to the WwTWs and/or the introduction of new treatment technologies with a performance equivalent or above to microfiltration - reverse osmosis. This could be particularly appropriate where existing wastewater

treatment processes only achieve a low fractional removal up to 0.6 for substances such as diclofenac, propranolol, glyphosate, EE2 and dissolved metals. Or in situations where removal is already significant (>0.90) for substances including triclosan, ibuprofen, BDE47, tributyltin, benzo(g,h,i)perylene, and it is unlikely that any incremental change to the current process will produce the required improvement.

5. Conclusions

For all the groups of chemicals variable removal was observed nationally, which was not exclusively related to the type of biological treatment process at individual treatment works. There were examples of each type of biological process which performed well in terms of removal of chemicals and others where removals were lower. However, the reasons for this variation are not immediately apparent. Variation could be due to flows and load variation within catchments or design and operation of individual works. Nevertheless, it is evident from this national survey that incremental improvements in the removal of trace chemicals might be possible by optimising operation. This would be particularly relevant for works that are operating close to EQS requirements where a marginal improvement achieved through process optimisation could result in compliance. On the other hand step changes in performance, for example an order of magnitude reduction in concentrations, clearly require new additional treatment or source control measures.

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Table 1 Summary of process type, final effluent consent, flow and dilution* for the 16 wastewater treatment works.
 *based on mean effluent flow versus mean river flow

WwTW code	Population equivalent	Key process information	Consent levels	Consented flow (m³/d)	Dilution
1	30,278	nitrifying, biological filtration	ammonia: 20 mg/l	6,138	marine
2	71,597	non-nitrifying, biological filtration	ammonia: 3 mg/l; phosphorus: 2 mg/l	14,300	6
3	3,424	nitrifying, biological filtration	ammonia: 10 mg/l	740	2
4	16,053	nitrifying, biological filtration	ammonia: 10 mg/l; phosphorus: 2 mg/l	2,950	1
5	47,569	non-nitrifying, biological filtration	phosphorus: unknown	12,000	20
6	25,397	Biological filtration: nitrifying	ammonia (summer): 10mg/l; ammonia (winter): 15 mg/l	4,784	130
7	203,133	nitrifying, biological filtration	ammonia: unknown	72,000	1
8	205,935	nitrifying, activated sludge	ammonia: 5 mg/l	65,000	18
9	122,127	nitrifying, activated sludge process, filters for Phosphorus and solids removal	ammonia: 5 mg/l; phosphorus: 2 mg/l	10,800	10
10	66,205	BNR	ammonia (summer): 5mg/l; ammonia (winter): 10 mg/l; phosphorus: 2 mg/l	21,500	2
11	95,415	nitrifying, activated sludge process	ammonia (summer): 5 mg/l; phosphorus: 1 mg/l	22,600	6
12	139,411	nitrifying, activated sludge process, UV disinfection	details of consents unknown; UV to achieve pathogen kill	40,486	marine
13	46,878	activated sludge process, primary sedimentation	ammonia: unknown	16,040	7
14	71,950	non-nitrifying, activated sludge process	BOD/SS: 75/100 mg/l; ammonia (composite); 15-44 mg/l; ammonia (instantaneous): 45mg/l	26,100	25
15	12,903	pre-screening and six MBRs	details of consents unknown	4,910	marine
16	31,637	activated sludge process, no upstream sedimentation	BOD/SS: 35/100 mg/l; ammonia: 35 mg/l; SRP: 2 mg/l	11,600	marine

Table 2 Statistical summary of sewage influent characteristics

Sanitary parameters (mg/L)	25%ile	median	mean	75%ile	Std. dev.	CoV
Total suspended solids	195	288	296	379	109	0.37
Ammoniacal nitrogen NH ₄	33	46	46	58	13	0.28
TON as NO ₃	2.4	2.9	4.2	4.4	3.9	0.91
BOD	219	267	279	326	71	0.25
Chemical Oxygen Demand	537	673	665	779	150	0.23
Total phosphorus (as P)	7	8	8	9	2	0.23
Orthophosphate (as PO ₄)	12	14	14	18	5	0.36
Metals (µg/L)						
aluminium (dissolved)	20	40	54	51	53	0.98
aluminium (total)	905	1470	1722	2071	1163	0.68
aluminium (reactive)	8	12	16	18	12	0.78
iron (dissolved)	88	215	253	287	207	0.82
iron (total)	648	1097	2483	2384	3142	1.27
cadmium (dissolved)	0.07	0.10	0.37	0.12	1.04	2.80
cadmium (total)	0.28	0.45	0.57	0.57	0.55	0.98
nickel (dissolved)	3.9	6.3	9.1	13.5	7.4	0.82
nickel (total)	7	11	14	17	10	0.74
copper (dissolved)	11	17	23	23	25	1.10
copper (total)	44	65	76	89	48	0.62
lead (dissolved)	1.3	2.0	2.1	2.5	1.1	0.53
lead (total)	8	12	17	20	16	0.96
mercury (dissolved)	0.011	0.014	0.015	0.018	0.005	0.35
mercury (total)	0.025	0.053	0.066	0.087	0.055	0.82
zinc (dissolved)	30	37	41	48	18	0.44
zinc (total)	134	160	180	234	72	0.40
Regulated and emerging organic chemicals (µg/L)						
glyphosate	0.5	0.6	0.9	0.9	0.6	0.74
AMPA	1.1	1.8	1.9	2.5	1.1	0.57
bentazone	0.01	0.04	0.04	0.06	0.04	0.86
mecoprop	0.03	0.05	0.05	0.08	0.03	0.65
anthracene	0.03	0.05	0.06	0.08	0.03	0.47
fluoranthene	0.08	0.11	0.13	0.15	0.07	0.54
naphthalene	0.9	1.1	1.5	1.3	1.5	1.03
benzo(a)pyrene	0.02	0.02	0.04	0.04	0.04	0.98
benzo(b)fluoranthene	0.01	0.02	0.04	0.05	0.05	1.08
benzo(k)fluoranthene	0.02	0.02	0.03	0.04	0.02	0.70
benzo(g,h,i)perylene	0.016	0.026	0.132	0.255	0.180	1.36
indeno(1,2,3-cd)pyrene	0.018	0.020	0.107	0.073	0.158	1.48
BDE47	0.0064	0.0085	0.0088	0.0099	0.0037	0.42

Sanitary parameters (mg/L)	25%ile	median	mean	75%ile	Std. dev.	CoV
BDE99	0.0074	0.0107	0.0105	0.0129	0.0049	0.47
bisphenol-A	0.68	1.07	2.05	1.35	3.40	1.66
diethylhexylphthalate	10.4	14.8	17.8	20.9	9.6	0.54
EDTA	258	581	585	818	360	0.62
Nonylphenol	2.4	3.0	3.4	3.6	2	0.61
Tributyltin	0.0033	0.0045	0.0052	0.0052	0.0043	0.83
triclosan	2.1	2.5	2.5	2.9	0.6	0.23
Pharmaceuticals (µg/L)						
ibuprofen	11	15	14	18	4	0.31
diclofenac	0.3	0.7	1.5	1.7	1.9	1.25
propranolol	0.20	0.25	0.26	0.31	0.09	0.33
fluoxetine	0.05	0.06	0.07	0.10	0.03	0.39
erythromycin	1.5	2.0	2.0	2.3	0.8	0.42
ofloxacin	0.03	0.08	0.18	0.17	0.33	1.78
oxytetracycline	2.1	2.8	3.6	4.6	2.5	0.70
salicylic acid	34	48	52	60	26	0.50
oestrone	0.036	0.045	0.049	0.061	0.013	0.27
17β-oestradiol	0.015	0.020	0.020	0.024	0.0050	0.25
17α-ethinylestradiol	0.0007	0.0008	0.0010	0.0012	0.0004	0.41

CoV is between works coefficient of variation

Table 3. Loadings of variables on principal components 1 to 4

	Component			
	1	2	3	4
Variance	36.1%	17.8%	14.3%	12.8%
IBPF	.927			
TRICL	.840			
E2	.738	.571		
BDE47	.710		-.512	
CUT	.604	-.455		
TBT	.553	-.588	.406	
OXTCY	.524		-.665	
BGHIP	.507	.490		
ZNT	0	-.663		.427
PRPL	0			.831
EE2	0		.722	
dcf	-.517	.446		.654

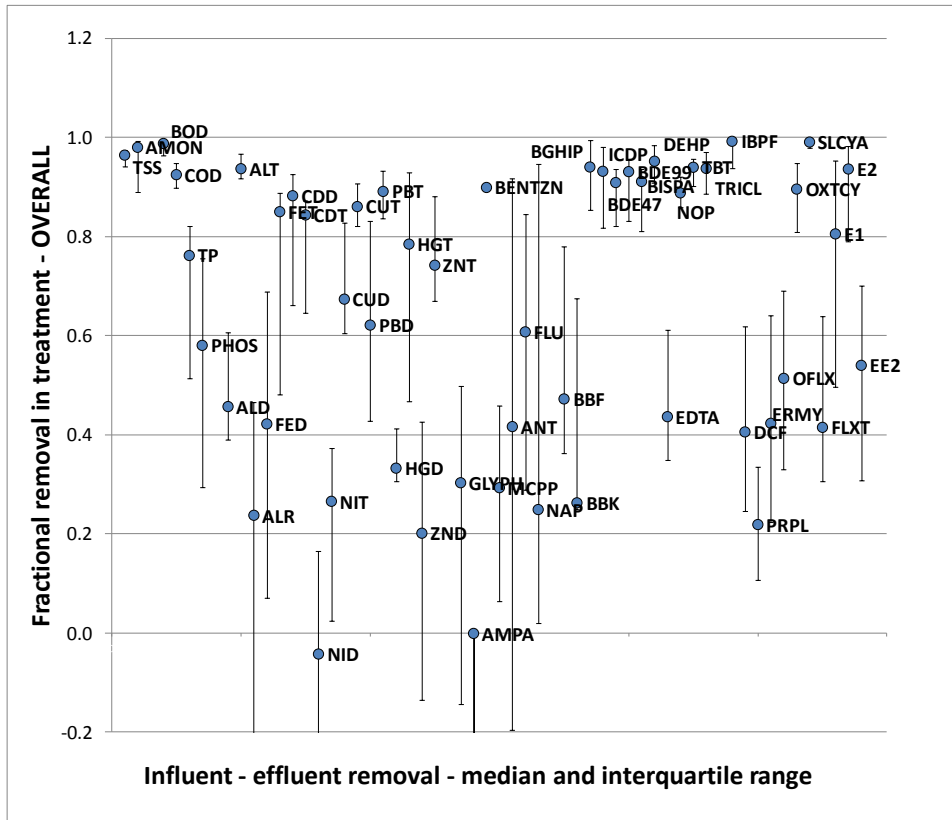


Figure 1 Fractional removal across the entire treatment process (influent to effluent)

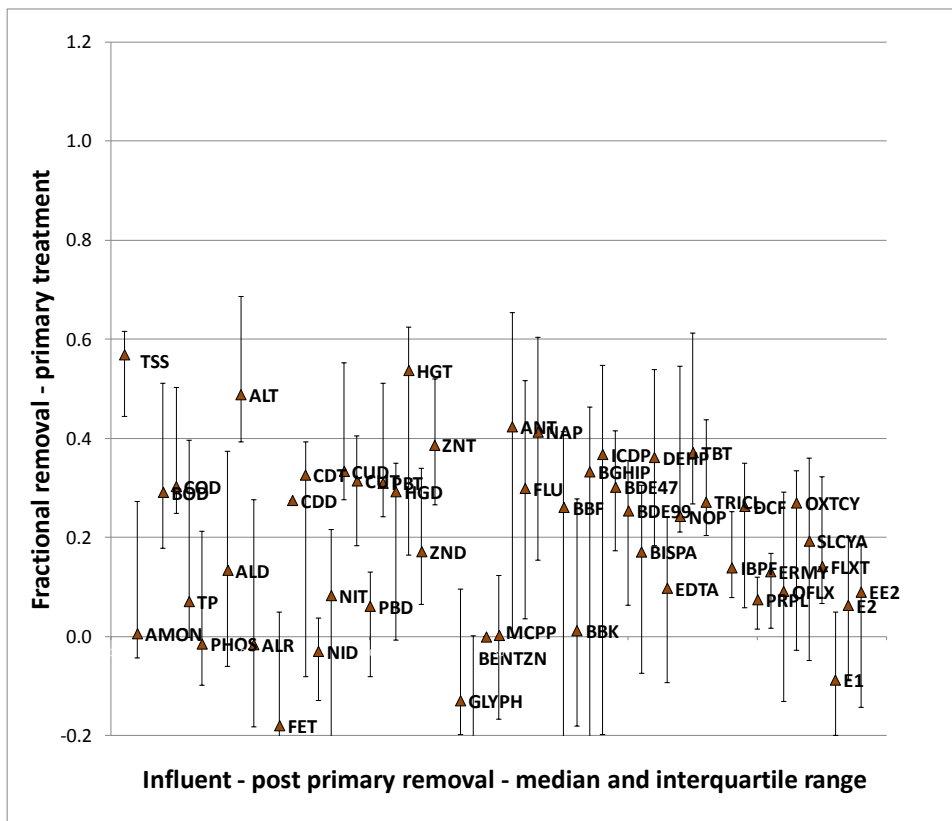
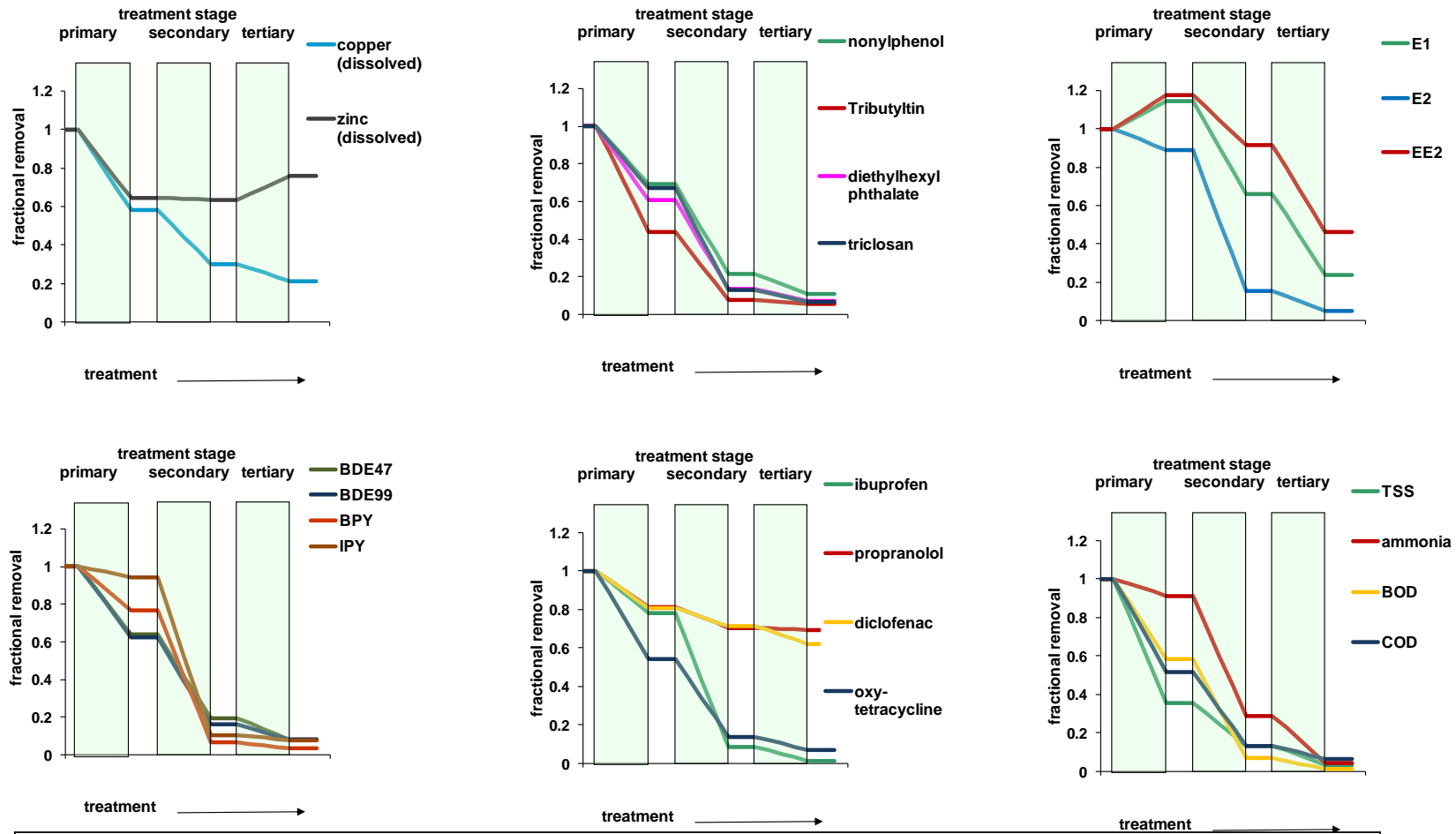


Figure 2 Fractional removal across primary sedimentation (influent to settled sewage)



Note to Figure 3: The far right hand side of the diagram indicates the percentage of the input that is discharged. Six different classes of substances are illustrated – from top left to bottom right: two important metals, four industrial chemicals, three steroids, PAHs and BDEs, pharmaceuticals and sanitary determinands.

[Key: BDE brominated diphenyl ethers, BPY benzo(ghi)perylene, IPY indeno (cd) pyrene, E1 estrone, E2 estradiol, EE2 ethinyl estradiol]

Figure 3 Fractional removals in primary, secondary and tertiary wastewater treatment

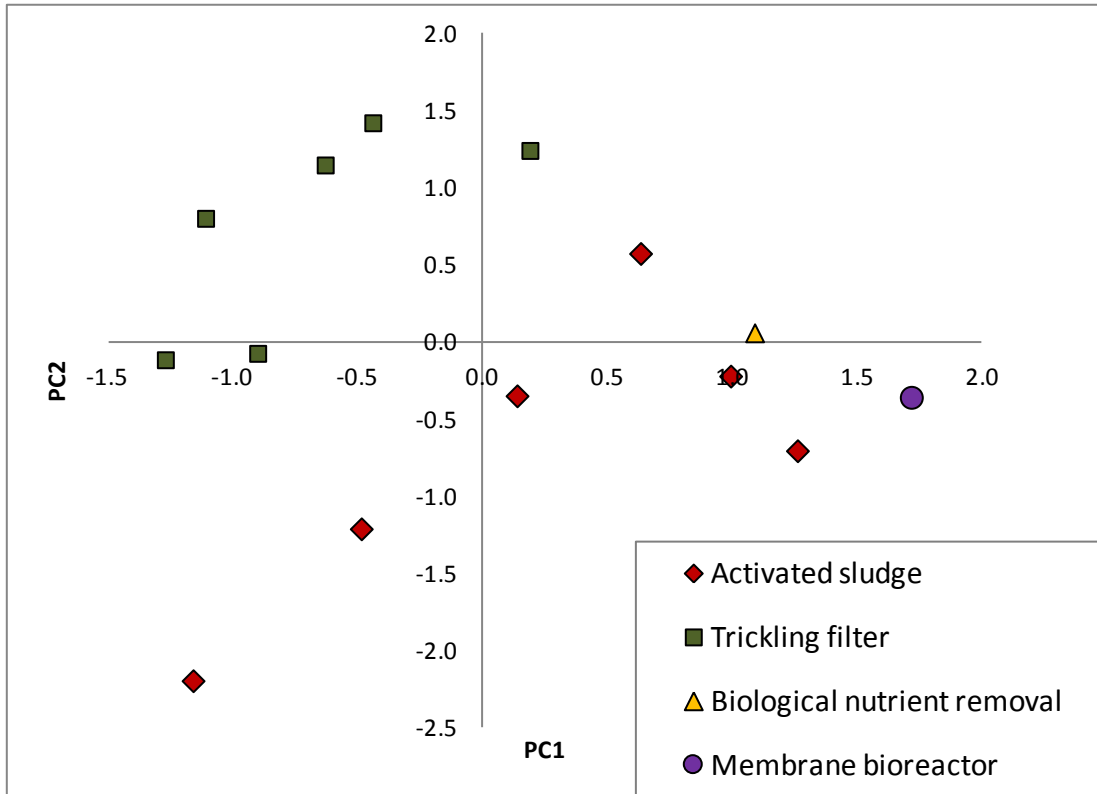


Figure 4. Results of principal components analysis, works by treatment type along PC1 and PC2.

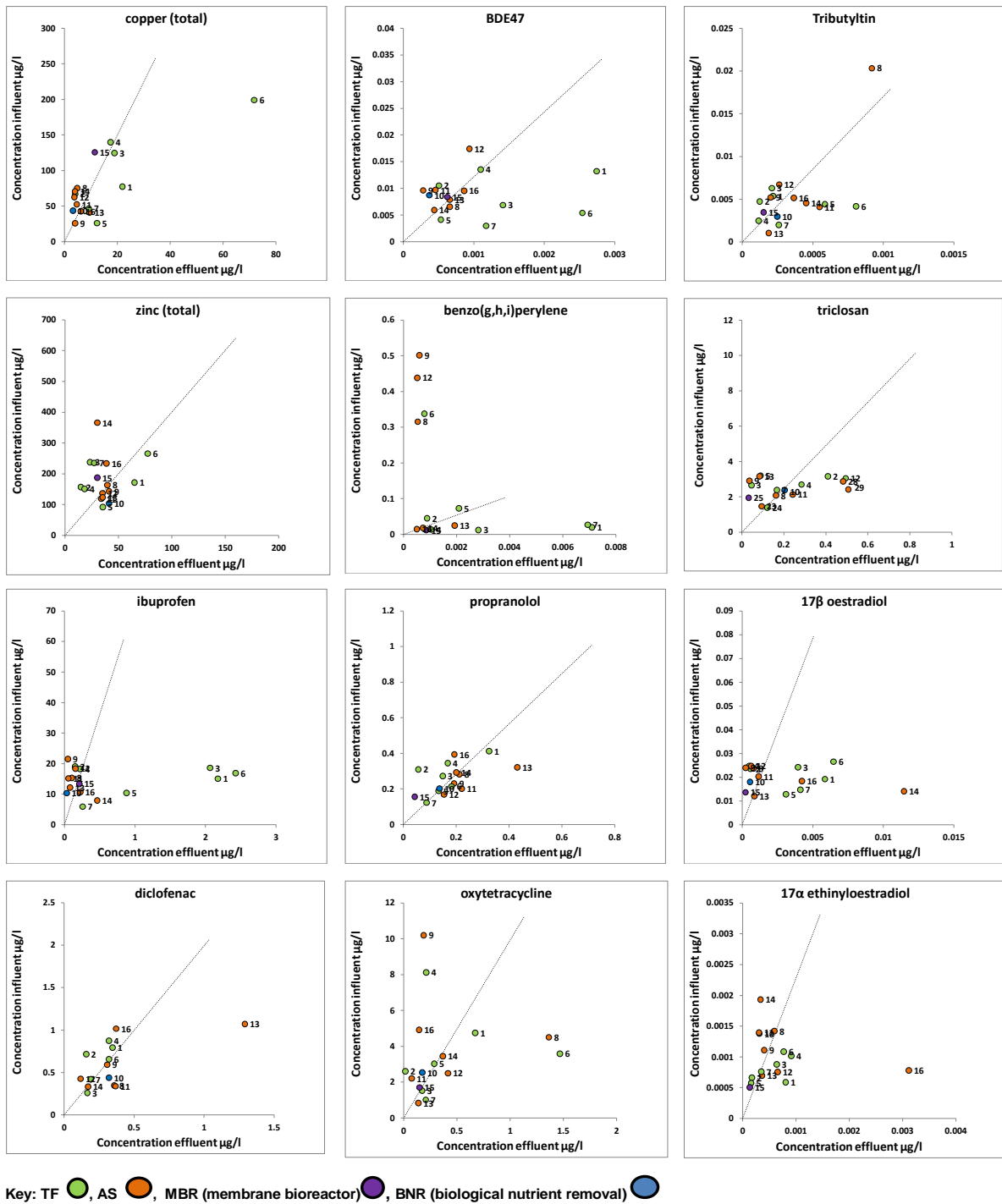


Fig. 5. Comparison of influent and effluent concentrations.