

Distribution of trace metals (Cu, Pb, Ni, Zn) between particulate, colloidal and truly dissolved fractions in wastewater treatment

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Abstract

The distribution of Cu, Pb, Ni and Zn between particulate, colloidal and truly dissolved size fractions in wastewater from a trickling filter treatment plant was investigated. Samples of influent, primary effluent, humus effluent, final effluent and sludge holding tank returns were collected and separated into particulate (i.e. > 0.45 μm), colloidal (i.e. 1 kDa to 0.45 μm), and truly dissolved (i.e. < 1 kDa) fractions using membrane filters. In the influent, substantial proportions of Cu (60%), Pb (67%), and Zn (32%) were present in the particulate fraction which was removed in conjunction with suspended particles at the works in subsequent treatment stages. In final effluent, sizeable proportions of Cu (52%), Pb (32%), Ni (44%) and Zn (68%) were found within the colloidal size fraction. Calculated ratios of soluble metal to organic carbon suggest the metal to be adsorbed to or complexed with non-humic macromolecules typically found within the colloidal size range. These findings suggest that technologies capable of removing particles within the colloidal fraction have good potential to enhance metals removal from wastewater.

Keywords: wastewater; membrane filtration; colloids; trace metals; particle fractions

1. Introduction

Wastewater treatment plants (WWTPs) receive metal inputs from both domestic and industrial sources, such that their discharges may cause harm in receiving waters (Stumm and Morgan, 2012). As a consequence of their potential to cause harm, there are regulatory drivers that require metals such as Cu, Pb, Ni and Zn to be removed as part of the wastewater treatment process. In the United States, the Clean Water Act defines Criteria Maximum Concentrations (CMC) and Criterion Continuous Concentrations (CCC) for heavy metals to protect aquatic life and human health in surface water (EPA,

2016). Hardness-based standards are currently used to assess compliance for Pb, Ni and Zn, however, since 2007 standards for Cu in the United States have been determined using the biotic ligand model, which uses site specific information on physico-chemical characteristics to convert a dissolved phase metal concentration into an equivalent bioavailable concentration (EPA, 2016). Within the European Union, the Water Framework Directive (WFD) (2000/60/EC) has recently specified bioavailability-based standards for Pb and Ni which are classified as Priority Hazardous Substances. Bioavailability-based standards have also been specified for Cu and Zn, classified as Specific Pollutants under the WFD, in the United Kingdom (UKTAG, 2008). Whilst improving the environmental relevance, bioavailability-based standards are, nonetheless, expected to significantly reduce acceptable metal concentrations (Peters et al. 2009). It is, however, difficult to reliably reduce trace metal concentrations in wastewater and studies have shown that WWTP removal efficiencies vary considerably, regardless of the treatment/removal technology applied (Gardner et al. 2013; Ziolkowski et al. 2011).

The trickling filter treatment process is one of the oldest approaches used to treat wastewater, and, due to their low energy consumption and relative simplicity, is still the most common treatment process applied in small and medium sized WWTPs in the United Kingdom (Marquet et al. 2007). Hence, the ability to improve the metal removal performance of this treatment type will present a significant opportunity to reduce metal inputs to receiving waters. Trickling filter treatment involves dripping wastewater over media where microorganisms grow in a biofilm. Microorganisms produce and secrete extra-cellular polymeric substances (EPS), which are high molecular weight polysaccharides and proteins with which metals can complex with (Sheng et al. 2013). Nevertheless, information about the behaviour of metals at trace level concentrations within the trickling filter process is scarce, possibly owing to difficulties in sampling the biomass. As such, the exact mechanism of metal removal by the biological film in trickling filters remains to be established (Ziolkowski et al. 2011). A study by Marquet et al. (2007), however, found that the performance of trickling filters was sensitive to the concentration of particles with a size between 1 and 50 μm . Such behaviour was linked to the proportion of colloidal material in the feed, thus gaining insight into the nature and size of particles throughout the wastewater

treatment process could offer an opportunity to improve trickling filter performance with regard to metal removal.

Metals are traditionally considered to exist in two size fractions: a soluble fraction that passes through a filter with a pore size of 0.45 μm , and a particulate fraction which is retained on the filter (i.e. $> 0.45 \mu\text{m}$). Cu and Pb are known to have a high affinity for the particulate fraction and therefore can be removed via physical separation (Choubert et al. 2011). Conversely, Ni and Zn dominate in the soluble fraction, which is typically comprised of free metal ions, complexed metal, and metal entrained within colloidal suspensions (Schijf and Zoll, 2011; Worms et al. 2010a). In this case, adsorption/ion exchange processes or chemical modification are required for effective metal elimination (Martin et al. 1995).

Material within the soluble fraction can be separated into two further size fractions namely, a colloidal fraction, which encompasses material found in the size range 1 kDa to 0.45 μm , and a truly dissolved fraction, which is composed of constituents with a molecular weight $< 1 \text{ kDa}$ (Worms et al. 2010a). Metal distribution within the soluble fraction is influenced by the presence of functional groups (ligands) that may complex metal ions and, as such, the quantity and type of dissolved organic carbon (DOC) exerts an important influence on trace metal speciation (Ma et al. 2001). Whereas the concentration of DOC (usually in mg/L) quantifies the amount of organic matter present in wastewater the role of DOC in the behaviour of metals within effluent is not well understood (Worms et al. 2010a). Furthermore, DOC is seldom measured in WWTPs (Katsoyiannis and Samara, 2007).

Studies on the characterisation of organic matter have found that the truly dissolved size fraction ($< 1 \text{ kDa}$) is primarily composed of humic substances, which contribute from 3 to 28% of the DOC in effluents (Imai et al. 2002). Amino acids, carbohydrates, synthetic ligands such as EDTA, and hydrated metal ions have also been found within this size fraction (Shon et al. 2006a). In contrast, organic matter in the colloidal size fraction (1 kDa to 0.45 μm) is predominantly composed of non-humic macromolecules including proteins, polysaccharides and aminosugars (Jarusutthirak et al. 2002) to which metals may adsorb or complex with in wastewater (Sheng et al. 2013). The presence of this

colloidal material may confound traditional assumptions about how metals behave in solution (i.e. mechanisms other than complexation). Additionally, the lack of distinction between colloidal materials and other dissolved phase materials has limited the design and performance of wastewater treatment processes (Tchobanoglous et al. 2003).

Studies on the distribution of metals in WWTP effluents, those operating trickling filters in particular, are limited to conventional classification (i.e. soluble and particulate). Such simplified approach limits an understanding of those mechanisms influencing metal speciation in wastewater (Buzier et al. 2006). This is of particular importance as the removal of both soluble and particulate metal fractions during wastewater treatment will be necessary in order to comply with more stringent discharge quality requirements and environmental quality standards (Ziolko et al. 2009).

The aim of this study was to investigate the behaviour and fractionation of trace metals (Cu, Pb, Ni and Zn) in effluent from a works operating trickling filter treatment in order to better understand the potential options to enhance metal removal.

2. Material and methods

2.1 Study site

The effluent examined in this study was obtained from a WWTP located in the UK which serves an urban catchment population treating, on average, 432,000 m³ of influent per day. Contributors to the metal load entering the works include metals corroded from the domestic water supply infrastructure, leaching of metal from household plumbing and inputs from diffuse sources, such as urban run-off. Influent is initially subject to screening and grit removal processes, followed by primary settling tanks and trickling filters. Tertiary treatment involves a nitrifying submerged aerated filter (N-SAF), which has the function of removing ammonia, and DynaSand[®] filters which polish the effluent prior to discharge in the receiving water (Fig. 1).

2.2 Sampling and analysis

Samples were collected over a 12-month period (February 2015 to January 2016) from a number of treatment stages at a trickling filter plant, namely; influent, primary effluent, humus effluent, final effluent and sludge holding tank (HT) returns (Fig. 1). Grab samples of wastewater were taken at least once each month. Grab samples of sludge HT returns were taken a minimum of every 4 months. Samples were stored in a cool box during transport and were stored at 4 °C in the laboratory.

In situ analysis of temperature, pH and redox potential was conducted with a HANNA (HI 98120) probe (APHA, 2005). Suspended solids were separated with standard vacuum filtration equipment (APHA, 2005). Total COD was determined by COD cell test kits (Fisher Scientific, Leicestershire, UK).

Particle size fractionation of the samples was conducted following a variation of the method described by Barker and Stuckey (1999). Initial fractionation of samples involved vacuum filtration (APHA, 2005) through 0.45 µm polyethersulphone membranes (Millipore, Livingston, UK) to obtain the soluble phase. Regenerated cellulose membranes (Millipore, Livingston, UK) were used to fractionate samples into low molar mass (LMM) colloidal (100 kDa) and so-called truly dissolved (1 kDa) phases. All membranes were washed in sequences of ultrapure water (0.05 µS conductivity level), 0.01 M NaOH (reagent grade, Fisher Scientific, Loughborough, UK) and 0.01 M HCl (reagent grade, Fisher Scientific, Loughborough, UK). This alkaline/acid cleaning sequence was repeated after each use; subsequently the membranes were stored in a 10 % ethanol solution (reagent grade, Sigma-aldrich, Gillingham, UK). LMM colloidal and truly dissolved fractionations were obtained by operating an Amicon 8400 stirred pressure cell (Millipore, Livingston, UK). Filtration was driven by nitrogen gas at a pressure of 20 kPa for 100 kDa membranes and 160 kPa for 1 kDa membranes. In all instances, samples were filtered progressively through the series of membranes. The membrane cell was stored in a 2% nitric acid bath (reagent grade, Fisher Scientific, Loughborough, UK) between uses and all plastic and glassware were alkaline and acid washed before being stored in 2% nitric acid. Concentration polarisation was limited through the operation of an integrated bar stirrer, whilst the adopted filtrate/retentate ratio was 0.4.

Fractionated samples were analysed for DOC with a TOC-V analyser (Shimadzu, Milton Keynes, UK). Target metals (Cu, Pb, Ni and Zn) were measured with an ELAN 9000 inductively coupled plasma-mass spectrometer (ICP-MS) (Perkin Elmer, Beaconsfield, UK). The limit of detection for all the metals was 0.01 µg/L. The accuracy for all metals, expressed as % of recovery, was comprised between 92% and 108%. To determine the total concentration of each target metal by ICP-MS, unfiltered samples were digested with a CEM-MARS microwave (CEM, Buckingham, UK). Sample blanks were processed through the preparation and analytical procedures conducted in order to account for any background contribution of the target metals.

Phase distributions were calculated as follows:

particulate = total - soluble,

high molar mass (HMM) colloidal = soluble - LMM colloidal,

LMM colloidal = LMM colloidal - truly dissolved.

Statistical analysis of the obtained data was done with the software package Minitab 17. One-way ANOVA tests were performed to assess the differences in metal presence and phase distribution between samples. Pearson's correlation coefficient tests were used to identify relationships between the concentration of metals and total suspended solids (TSS). Correlation strength was determined to be weak (0.2-0.39), moderate (0.4-0.59) or strong (> 0.59) using guidance from Evans (1996). Both tests were conducted with a level of significance $p < 0.05$.

3. Results and discussion

3.1 Works performance

The concentrations and rates of removal found across different treatment stages for the considered determinands are summarised in Table 1.

The overall rates of removal for TSS (95%) and COD (86%) indicated that operating conditions at the WWTP were typical and in line with expectations for treatment works of this type (Table 1). Influent and final effluent concentrations of these determinands were also within the range reported for trickling filter works in the United Kingdom (Gardner et al. 2013).

At the plant, limited DOC elimination was observed in primary treatment (16%) since this stage is responsible for the removal of particulate matter. During secondary treatment a 48% DOC removal was, however, within the range (40-66%) reported by Confer et al. (1995) for a works operating trickling filter treatment. Discharge concentrations were also comparable to values reported for other WWTPs (Shafer et al. 1998).

The abundance of target metals in terms of total concentration followed the order $Zn > Cu > Ni > Pb$ (see Table 1). The concentrations of trace metals found in the influent were similar to those reported by other investigators at WWTPs elsewhere (Table S1). Additionally, final effluent metal concentrations were comparable to values reported in other UK studies (Gardner et al. 2013).

3.2 Whole works effect on the phase distribution of metals in wastewater

The metal concentrations observed in the LMM colloidal and HMM colloidal fractions showed a high level of variability, such that, no statistically significant differences between these fractions could be detected (one-way ANOVA, $p > 0.05$). Consequently, these fractions were combined into a single colloidal size fraction (from 0.45 μm to 1 kDa). The distribution of target metals within the particulate, colloidal and truly dissolved fractions at different treatment stages are presented in Fig. 2.

3.2.1 Cu and Pb

Good overall rates of removal were observed for Cu (60%) and Pb (58%) at the site studied (Table 1). For the particulate fraction in particular, a high level of removal occurred as indicated by significantly

lower concentrations of Cu ($p < 0.001$) and Pb ($p < 0.001$) found in the final effluent (Table 1). Strong correlations were observed between TSS and particulate phase metal concentrations for Cu ($r = 0.732$, $p < 0.001$) and Pb ($r = 0.727$, $p < 0.001$), which indicate that removal of both metals occurred in conjunction with the elimination of suspended particles. The proportion of Cu and Pb in the particulate fraction in the influent and the overall rate of removal that was observed was similar to that found in other studies (Karvelas et al. 2003; Shafer et al. 1998).

Appreciable amounts of Cu (28%) and Pb (27%) were found in the colloidal fraction of the influent (Fig. 2a). Although colloidal removal for these metals was significant, as p values were 0.001 and less than 0.001 for Cu and Pb respectively, residual concentrations of Cu (8.8 $\mu\text{g/L}$) and Pb (0.3 $\mu\text{g/L}$) remained in the colloidal fraction following treatment (see Fig. 2d). This finding was in line with expectation, as soluble Cu and Pb typically adsorb onto the surface of colloidal materials (Martin et al. 1995). Furthermore, other studies have shown a large proportion of Cu to exist within similar colloidal size fractions in final effluent. For example, Shafer et al. (1998) observed 30% distribution of Cu within the size fraction 10 kDa to 0.22 μm . Worms et al. (2010a) found substantial proportions of Cu and Pb in the colloidal size fraction (0.45 μm -1 kDa) and reported that the distribution of metals between colloidal and truly dissolved fractions was strongly influenced by the distribution of DOC within these same fractions. DOC is composed of organic compounds with functional groups (ligands) that have a high affinity for metal ions (Constantino et al. 2015; Sarathy and Allen, 2005). The distribution of DOC within wastewater at the site studied (see Fig. 3) was greater in the colloidal fraction compared with the truly dissolved fraction, as found in effluents elsewhere (Worms et al. 2010b). To compare the relative affinity of the target metals for organic ligands in the soluble fraction, the molar ratios of metals to organic carbon were calculated in final effluent at the WWTP (see Table 2). This analysis found that the proportions of Cu (79%) and Pb (71%) were highest in the colloidal fraction. Other studies have found that the colloidal size fraction is predominantly composed of non-humic macromolecules, such as polysaccharides, proteins and aminosugars, to which metals can adsorb to or complex with (Jarusutthirak et al. 2002; Sheng et al. 2013; Shon et al. 2006a). Hence, the findings from the present

study suggest that a sizeable proportion of Cu and Pb may be adsorbed to or complexed with macromolecules present in the colloidal size fraction.

Compared with particulate and colloidal fractions, a relatively small proportion of Cu (12%) and Pb (7%) were observed in the truly dissolved size fraction of the influent (Fig. 2a). For Pb, no statistically significant difference was observed between influent and final effluent ($p = 0.082$). Truly dissolved Cu concentrations were significantly lower in final effluent ($p = 0.026$), although Cu removal from this fraction was negligible (2%). This suggests that the treatment technologies operating at the works had little or no effect on Cu and Pb found within this fraction (Fig. 2d). In fact, other studies (Imai et al. 2002; Shon et al. 2006a) have identified that the truly dissolved fraction in wastewater comprises free metal ions and organic constituents, including amino acids, carbohydrates, synthetic ligands (such as EDTA) and humic substances, which metals may adsorb too and/or complex with. These organics are known to be recalcitrant (Lipczynska-Kochany and Kochany 2009; Snyder et al. 2004) so that negligible removals for metals associated to them can be expected.

3.2.2 Ni and Zn

As shown in Fig. 2a, Ni and Zn were predominantly found in the colloidal fraction of the influent with sizeable proportions in particulate form, this is, 39% for Ni and 32% for Zn. Additionally, small amounts of Ni (18%) and Zn (9%) were observed in the truly dissolved phase.

A low overall rate of removal (28%) was observed for Ni (see Table 1), with no significant correlation identified between particulate Ni and TSS concentrations ($r = 0.222$, $p = 0.101$). This metal is highly soluble and, because of its low affinity for suspended matter (Karvelas et al. 2003), its removal during wastewater treatment is low (Schafer et al. 1998), especially when compared with Cu, Pb and Zn (see Table 1). Although particulate Ni concentrations were significantly lower in the final effluent ($p = 0.012$), only a small amount of Ni (29%) was removed from this fraction. In addition, Ni concentrations measured in the colloidal ($p = 0.073$) and truly dissolved ($p = 0.727$) fractions were not significantly different from those observed in the influent. These findings indicate that Ni persists after

treatment with little or no change in its distribution between particle size fractions (see Fig. 2d). Such behaviour was expected as other studies reported similar findings at WWTPs elsewhere (Karvelas et al. 2003).

Approximately half of the initial Zn load was removed at the site (Table 1). A moderate correlation was observed between particulate phase Zn and TSS concentrations ($r = 0.480$, $p < 0.001$) with a significantly lower Zn concentration ($p < 0.001$) observed in the particulate fraction of final effluent. These findings indicate that Zn, albeit to a lesser degree than Cu and Pb, has some affinity for suspended particles in wastewater as reported by Karvelas et al. (2003). Elimination of Zn from the particulate fraction was accompanied by removal, to a lesser degree, from the colloidal fraction. As such, an increase in the ratio of colloidal to particulate Zn was observed in final effluent (see Fig. 2d). In the truly dissolved fraction no significant change ($p = 0.060$) was measured, thus indicating that Zn in the truly dissolved fraction remained as for Cu, Pb and Ni.

Residual amounts of Zn as well as Ni were predominantly found in the colloidal size fraction of the final effluent (see Fig. 2d). This was unexpected since Ni and Zn are highly soluble in wastewater and, given what is understood of their thermodynamic properties (i.e. slow rate of reaction, low stability constants), a large proportion of soluble Ni and Zn was expected to remain unbound in the free ionic form and distributed within the truly dissolved size fraction. Worms et al. (2010) reported, however, that Ni and Zn can interact with colloidal organic materials in the colloidal size fraction ($0.45 \mu\text{m}^{-1}$ kDa). At the site studied, calculated molar ratios of soluble metals to organic carbon indicate that dissolved species in the colloidal size range are relevant for the binding of Ni and Zn (see Table 2). Compared with other target metals, more Ni (36%) was found in the truly dissolved fraction although, similar to Cu and Pb, the highest relative proportions of Ni (64%) and Zn (74%) were found in the colloidal fraction (Table 2). This indicates that Ni and Zn may also be adsorbed to or complexed with macromolecules present in the colloidal size range. It is therefore plausible that removing organic materials within the colloidal size fraction could present an opportunity to reduce the concentrations of all target metals (Cu, Pb, Ni and Zn) in effluent discharges.

3.3 Effect of treatment stages on the phase distribution of metals in wastewater

3.3.1 Primary treatment

Comparable removal efficiencies for Cu, Pb, Ni and Zn were found in the primary settling tank at the site studied (see Table 1). In particular, removal of Cu (36%), Pb (30%), Ni (31%) and Zn (28%) occurred from the particulate fraction. These findings indicate that, when present in particulate form, metals readily settle during primary treatment, hence the comparable removal efficiencies observed for Cu, Pb, Ni and Zn regardless of the fraction (suspended or soluble) in which metals were predominantly found. Similar results were reported by Karvelas et al. (2003) who also found that the distribution of soluble to particulate metal increased in primary effluent as herein shown in Fig. 2 for Cu, Pb and Ni.

3.3.2 Secondary treatment

Good removals for Cu (32%) and Pb (36%) were achieved at the secondary treatment stage. In particular, substantial elimination of Cu (54%) and Pb (51%) from the particulate fraction was observed. Given that the trickling filter effectively removed TSS (63%) and that, when in particulate form, Cu and Pb were removed in conjunction with suspended particles, such results were anticipated.

Despite the removal of particulate Cu and Pb, only a small reduction in the proportion of these metals in the particulate fraction of humus effluent was observed (see Fig. 2c). This occurred as Cu (36%) and Pb (27%) were also removed from the soluble fraction at the secondary treatment stage. Within biological treatment, biomass produces and secretes EPS, a mixture of high molecular weight polysaccharides and proteins that can act as strong ligands for metals (Sheng et al. 2013). The strong affinity Cu and Pb have for EPS means these metals can dissociate readily from soluble complexes to undergo removal in association with biomass (Sheng et al. 2013).

Unlike Cu and Pb, no significant change in soluble concentrations of Ni or Zn was observed, owing to the lower affinity these metals have for EPS (Comte et al. 2006; Savvaidis et al. 2003), thus accounting for the comparably lower removal efficiencies trickling filter treatment achieved for Ni and Zn (see Table 1). In fact, during biological treatments direct settling is suggested to be of greater

significance for the removal of Ni and Zn (Stephenson and Lester, 1987). This was the case for Zn at the works studied with significantly lower particulate phase Zn ($p < 0.001$) concentrations measured in humus effluent, accounting for the good rate of removal (38%) from this fraction. Trickling filter treatment did, however, have no statistically significant influence on particulate phase Ni concentrations ($p = 0.92$).

3.3.3 Tertiary treatment

Good rates of removal were observed for Cu (35%) and Pb (37%) at the tertiary treatment stage, whilst a relatively moderate removal extent was measured for Zn (22%). In the particulate and colloidal fractions of final effluent significant decreases in the concentrations of Cu, Pb and Zn were observed. These findings were in line with expectation as, similar to primary and secondary treatment, a good rate of TSS removal (61%) was achieved, enabling removal of particulate metal in conjunction with suspended particles at the tertiary treatment stage. Furthermore, other studies (Mostafa and Aly, 2013) have identified that Dynasand[®] filters instigate the removal of particles by flocculation. This process encourages the agglomeration of colloidal materials, which metals may be adsorbed to or complexed with, into larger aggregates that are retained on the filter.

For Cu and Pb, decreases in concentrations of particulate and colloidal phase metal corresponded with an increase (12 to 22%) in truly dissolved distribution in final effluent (Fig. 2d). This finding was supported by significant increases in metal concentrations when comparing the truly dissolved fraction in humus effluent and final effluent samples for Cu ($p = 0.008$) and Pb ($p = 0.032$), indicating that release of these metals was occurring within tertiary treatment.

As the concentration of organics in the colloidal size fraction decreased from 12.4 to 8 mg/L, the DOC concentration within the truly dissolved phase increased from 3.5 to 5.3 mg/L. Since a substantial proportion of Cu (45%) and Pb (30%) was observed within the colloidal size fraction in humus effluent (Fig. 2c), the concentration of these metals increase in the final effluent as

suspended/colloidal organics become truly dissolved. Thus, suggesting that the release of metals was influenced by DOC removal in the tertiary treatment stage.

Nevertheless, the relationship between metals and DOC release reflects only a weak correlation for both Cu ($r = 0.299$) and Pb ($r = 0.254$), which suggests that DOC is not the only contributing parameter toward metal release observed. The N-SAF process, included as part of tertiary treatment at the works (Fig. 1), could also contribute to metal release. In this process alkalinity consumption, owing to nitrification, lowers pH so that the presence of protons reduces the stability of metal complexes and enhances metal concentrations in the truly dissolved fraction.

A negligible overall rate of removal (1%) was recorded for Ni at the tertiary treatment stage (Table 1). In addition, little change was observed in the distribution of Ni between particle size fractions (see Fig. 2d), indicating that processes operated as part of tertiary treatment at the studied works had little effect on Ni.

3.4 Phase distribution of metals in sewage sludge

Within sludge returns, a proportion of each metal was observed within the particulate fraction, with Cu and Pb showing larger distributions when compared with Ni and Zn (Fig. 4). This occurs as Cu and Pb have a high affinity for particulate organic matter in sewage sludge (Garcia-Delgado et al. 2007). The greater abundance of Ni and Zn in the soluble fraction indicates that these metals have higher mobility within sludge, as reported by Ščančar et al. (2000). However, despite differing mobility, a similar distribution was found for Cu, Pb and Zn in the colloidal size fraction within sludge HT returns (Fig. 4). Sludge returns are expected to contain organic colloids with which metals can bind (Buzier et al. 2006) and metal complexation with soluble organic matter in sewage sludge has been reported elsewhere (Stylianou et al. 2007). In the presence of high divalent cation concentrations, such as those observed herein for Cu (143.1 $\mu\text{g/L}$), Pb (8.4 $\mu\text{g/L}$), Ni (38.4 $\mu\text{g/L}$) and Zn (223.5 $\mu\text{g/L}$), the structure of organic matter can change from a stretched linear configuration to a coiled and compact arrangement (Shon et al. 2006b). These structural alterations are thought to increase the availability of colloidal

material owing to the formation of protein-like aggregates that metals can adsorb to and/or complex with (Guibaud et al. 2003). Hence explaining why target metals were predominately found in the colloidal size fraction of the sludge returns (Fig. 4).

The relatively high proportion of Ni within the truly dissolved fraction compared with other metals studied (Fig. 4) has also been observed elsewhere (Ščančar et al. 2000). This occurs due to the higher selectivity of polyanions towards metals such as Cu for the formation of metal complexes, which in turn blocks functional groups (Ščančar et al. 2000). Blocking of functional groups has been found to reduce binding of Ni to a much greater extent than other metals so that a high proportion of this metal remains in the free ionic form (da Costa Cunha et al. 2015).

4. Conclusions

The experimental findings herein presented support the concept that particle size fractionation in wastewater helps to understand potential treatment options to enhance metal removal.

In sewage influent, Cu and Pb were predominantly observed in the particulate fraction. Removal from this fraction in subsequent treatment stages was strongly dependant on TSS elimination. During treatment, a sizable proportion of Zn in the influent was also found in the particulate fraction and showed moderate interaction with suspended particles; thus Zn and TSS removals were interdependent, albeit to a lesser degree than Cu and Pb. Because of a weak interaction with suspended particles, the overall rate of removal for Ni was not affected by TSS removal at the works.

After treatment, a substantial proportion of the residual Cu, Pb, Ni and Zn were found in the colloidal fraction of the final effluent. Calculated ratios of soluble metal to organic carbon in the final effluent determined that species in the colloidal size range had an important role in the binding of target metals. Such finding indicates that Cu, Pb, Ni and Zn may be adsorbed to or complexed with macromolecules (eg. proteins, polysaccharides, aminosugars etc.) typically present in the colloidal size fraction. Results from the present study therefore suggest that technologies capable of removing

particles within the colloidal size fraction could also reduce the concentrations of Cu, Pb, Ni and Zn in final effluent discharges.

Relative to colloidal and particulate fractions, only a small concentration of Cu, Pb, Ni and Zn was found in the truly dissolved fraction of influent and was not statistically different in final effluent. Hence treatment technologies operating at the studied works had little or no effect on metal found within the truly dissolved fraction.

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References

- APHA., 2005. Standard Methods for the Examination of Water and Wastewater. 21st ed. American Public Health Association: Washington, DC.
- Barker, D. J., & Stuckey, D. C. (1999). A review of soluble microbial products (SMP) in wastewater treatment systems. *Water Research*, 33(14), 3063-3082.
- Buzier, R., Tusseau-Vuillemin, M.H., dit Meriadec, C.M., Rousselot, O., & Mouchel, J.M. (2006). Trace metal speciation and fluxes within a major French wastewater treatment plant: impact of the successive treatments stages. *Chemosphere*, 65(11), 2419-2426.
- Choubert, J. M., Pomiès, M., Coquery, M., & Ruel, S. M. (2011). Influent concentrations and removal performances of metals through municipal wastewater treatment processes. *Water Science & Technology*, 63(9), 1967-1973.
- Comte, S., Guibaud, G., & Baudu, M. (2006). Biosorption properties of extracellular polymeric substances (EPS) resulting from activated sludge according to their type: soluble or bound. *Process Biochemistry*, 41(4), 815-823.
- Confer, D. R., Logan, B. E., Aiken, B. S., & Kirchman, D. L. (1995). Measurement of dissolved free and combined amino acids in unconcentrated wastewaters using high performance liquid chromatography. *Water Environment Research*, 67(1), 118-125.
- Constantino, C., Gardner, M., Comber, S. D. W., Scrimshaw, M. D., & Ellor, B. (2015). The impact of tertiary wastewater treatment on copper and zinc complexation. *Environmental Technology*, 36(22), 2863-2871.

da Costa Cunha, G., Goveia, D., Romão, L.P.C., & de Oliveira, L. C. (2015). Effect of the competition of Cu (II) and Ni (II) on the kinetic and thermodynamic stabilities of Cr (III)-organic ligand complexes using competitive ligand exchange (EDTA). *Journal of Environmental Management*, 154, 259-265.

Evans, J.D. (1996). *Straightforward statistics for the behavioral Sciences*. Brooks/Cole Publishing, Pacific Grove.

Environmental Protection Agency (EPA). (2016). Water quality criteria. Available at: <http://www.epa.gov/wqc> [Accessed on 2 March 2016].

García-Delgado, M., Rodríguez-Cruz, M.S., Lorenzo, L.F., Arienzo, M., & Sánchez-Martín, M.J. (2007). Seasonal and time variability of heavy metal content and of its chemical forms in sewage sludges from different wastewater treatment plants. *Science of the Total environment*, 382, 82-92.

Gardner, M., Jones, V., Comber, S., Scrimshaw, M.D., Coello-Garcia, T., Cartmell, E., & Ellor, B. (2013). Performance of UK wastewater treatment works with respect to trace contaminants. *Science of the Total Environment*, 456, 359-369.

Guibaud, G., Tixier, N., Bouju, A., & Baudu, M. (2003). Relation between extracellular polymers' composition and its ability to complex Cd, Cu and Pb. *Chemosphere*, 52(10), 1701-1710.

Houhou, J., Lartiges, B. S., Montarges-Pelletier, E., Sieliechi, J., Ghanbaja, J., & Kohler, A. (2009). Sources, nature, and fate of heavy metal-bearing particles in the sewer system. *Science of the Total Environment*, 407(23), 6052-6062.

Imai, A., Fukushima, T., Matsushige, K., Kim, Y. H., & Choi, K. (2002). Characterization of dissolved organic matter in effluents from wastewater treatment plants. *Water Research*, 36(4), 859-870.

Jarusutthirak, C., Amy, G., & Croué, J. P. (2002). Fouling characteristics of wastewater effluent organic matter (EfOM) isolates on NF and UF membranes. *Desalination*, 145, 247-255.

Karvelas, M., Katsoyiannis, A., & Samara, C. (2003). Occurrence and fate of heavy metals in the wastewater treatment process. *Chemosphere*, 53(10), 1201-1210.

Katsoyiannis, A., & Samara, C. (2007). The fate of dissolved organic carbon (DOC) in the wastewater treatment process and its importance in the removal of wastewater contaminants. *Environmental Science and Pollution Research-International*, 14(5), 284-292.

Kempton, S., Sterritt, R. M., & Lester, J. N. (1987). Heavy metal removal in primary sedimentation II. The influence of metal speciation and particle size distribution. *Science of the Total Environment*, 63, 247-258.

Lipczynska-Kochany, E., & Kochany, J. (2009). Effect of humate on biological treatment of wastewater containing heavy metals. *Chemosphere*, 77(2), 279-284.

Marquet, R., Muhammad, N., Vairavamoorthy, K., & Wheatley, A. (2007). Particle size distribution to assess the performance of trickling filters. *Process Safety and Environmental Protection*, 85, 99-103.

Ma, H., Allen, H. E., & Yin, Y. (2001). Characterization of isolated fractions of dissolved organic matter from natural waters and a wastewater effluent. *Water Research*, 35(4), 985-996.

Martin, J., Dai, M.H., & Cauwet, G. (1995). Significance of colloids in the biogeochemical cycling of organic carbon and trace metals in the Venice Lagoon (Italy). *Limnology and Oceanography*, 40, 119-131.

- Mostafa, H., & Aly, O.H.I. (2013). Comparison between rapid sand filter and dyna sand filter in wastewater tertiary treatment. *International Journal of Civil Engineering and Technology*, 4(6), 230-238.
- Peters, A., Merrington, G., & Brown, B. (2009). Using biotic ligand models to help implement environmental quality standards for metals under the Water Framework Directive. Science Report—SC080021/SR7b, 83.
- Rule, K. L., Comber, S. D. W., Ross, D., Thornton, A., Makropoulos, C. K., & Rautiu, R. (2006). Survey of priority substances entering thirty English wastewater treatment works. *Water and Environment Journal*, 20(3), 177-184.
- Sarathy, V., & Allen, H. E. (2005). Copper complexation by dissolved organic matter from surface water and wastewater effluent. *Ecotoxicology and Environmental Safety*, 61(3), 337-344.
- Savvaidis, I., Hughes, M. N., & Poole, R. K. (2003). Differential pulse polarography: a method for the direct study of biosorption of metal ions by live bacteria from mixed metal solutions. *Antonie van Leeuwenhoek*, 84(2), 99-107.
- Ščančar, J., Milačič, R., Stražar, M., & Burica, O. (2000). Total metal concentrations and partitioning of Cd, Cr, Cu, Fe, Ni and Zn in sewage sludge. *Science of the Total Environment*, 250, 9-19.
- Schijf, J., & Zoll, A. M. (2011). When dissolved is not truly dissolved—the importance of colloids in studies of metal sorption on organic matter. *Journal of Colloid and Interface Science*, 361, 137-147.
- Shafer, M. M., Overdier, J. T., & Armstrong, D. E. (1998). Removal, partitioning, and fate of silver and other metals in wastewater treatment plants and effluent-receiving streams. *Environmental Toxicology and Chemistry*, 17(4), 630-641.
- Sheng, G.P., Xu, J., Luo, H.W., Li, W.W., Li, W.H., Yu, H.Q., & Hu, F.C. (2013). Thermodynamic analysis on the binding of heavy metals onto extracellular polymeric substances (EPS) of activated sludge. *Water Research*, 47(2), 607-614.
- Shon, H.K., Vigneswaran, S., & Snyder, S.A. (2006a). Effluent organic matter (EfOM) in wastewater: constituents, effects, and treatment. *Critical Reviews in Environmental Science and Technology*, 36(4), 327-374.
- Shon, H. K., Vigneswaran, S., Kim, I. S., Cho, J., & Ngo, H. H. (2006b). Fouling of ultrafiltration membrane by effluent organic matter: a detailed characterization using different organic fractions in wastewater. *Journal of Membrane Science*, 278, 232-238.
- Snyder, S. A., Leising, J., Westerhoff, P., Yoon, Y., Mash, H., & Vanderford, B. (2004). Biological and physical attenuation of endocrine disruptors and pharmaceuticals: implications for water reuse. *Ground Water Monitoring and Remediation*, 24(2), 108-118.
- Soonthornnonda, P., & Christensen, E. R. (2008). Source apportionment of pollutants and flows of combined sewer wastewater. *Water Research*, 42(8), 1989-1998.
- Stephenson, T., & Lester, J. N. (1987). Heavy metal behaviour during the activated sludge process I. Extent of soluble and insoluble metal removal. *Science of the Total Environment*, 63, 199-214.
- Stumm, W., & Morgan, J.J. (2012). *Aquatic chemistry: chemical equilibria and rates in natural waters*. John Wiley and Sons, New York.

Stylianou, M.A., Kollia, D., Haralambous, K.J., Inglezakis, V.J., Moustakas, K.G., & Loizidou, M.D. (2007). Effect of acid treatment on the removal of heavy metals from sewage sludge. *Desalination*, 215, 73-81.

Tchobanoglous, G., Burton, F. L., & Stensel, H. D. (2003). *Wastewater engineering: treatment and reuse*. McGraw-Hill, Boston.

UK Technical Advisory Group (UKTAG). (2008). *UK environmental standards and conditions (phase 1)*.

Worms, I. A., Szigeti, Z. A. G., Dubascoux, S., Lespes, G., Traber, J., Sigg, L., & Slaveykova, V. I. (2010a). Colloidal organic matter from wastewater treatment plant effluents: Characterization and role in metal distribution. *Water Research*, 44, 340-350.

Worms, I. A., Traber, J., Kistler, D., Sigg, L., & Slaveykova, V. I. (2010b). Uptake of Cd (II) and Pb (II) by microalgae in presence of colloidal organic matter from wastewater treatment plant effluents. *Environmental Pollution*, 158(2), 369-374.

Ziolko, D., Hala, D., Lester, J. N., & Scrimshaw, M. D. (2009). The effectiveness of conventional trickling filter treatment plants at reducing concentrations of copper in wastewaters. *Science of the Total Environment*, 407(24), 6235-6241.

Ziolko, D., Martin, O.V., Scrimshaw, M.D., & Lester, J.N. (2011). An evaluation of metal removal during wastewater treatment: The potential to achieve more stringent final effluent standards. *Critical Reviews in Environmental Science and Technology*, 41(8), 733-769.

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