Article (refereed) - postprint

Peters, A.; Merrington, G.; Leverett, D.; Ellor, B.; Lofts, S.; Gravell, A. 2014. **The effect of advanced treatment of sewage effluents on metal speciation and (bio)availability**. *Bulletin of Environmental Contamination and Toxicology*, 92 (2). 248-252. 10.1007/s00128-013-1143-z

Title: The Effect of Advanced Treatment of Sewage Effluents on Metal Speciation and (bio)Availability

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ABSTRACT The bioavailability of metals can be strongly influenced by dissolved organic carbon (DOC). Wastewater treatment effluents add considerable quantities of DOC and metals to receiving waters, and as effluent controls become more stringent advanced effluent treatments may be needed. We assessed the effects of two types of advanced treatment processes on metal availability in wastewater effluents. Trace metal availability was assessed using Diffuse Gradients in Thin Films (DGT) and predicted through speciation modelling. The results show little difference in metal availability post-advanced treatment. EDTA-like compounds are important metal complexants in the effluents.

KEY WORDS freshwater, DOC, effluents, metals, bioavailability

There is an increase in regulatory concern in relation to the presence of trace levels of pharmaceutical and bioactive chemicals entering surface waters from sewage treatment plants (e.g. UBA 2011). Limit values for some pharmaceutical substances have been derived (EU Proposal 2011/0429) and limit values are routinely used to set permits and discharge limits. For water companies this presents considerable difficulties in terms of achieving the permitted limits.

In order to comply with these revised limits water companies are now considering advanced treatment options to remove these substances (e.g. Granular Activated Carbon (GAC) and ozone treatment). Such advanced effluent treatments have been shown to be effective at reducing effluent concentrations of a variety of micropollutants (Hollender et al. 2009), but may also have an effect upon the concentration, form, characteristics and metal binding capacity of the dissolved organic carbon (DOC) which is present in sewage effluents at high concentrations,

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owing to its removal, alteration or degradation during treatment (Winch et al. 2002).

DOC is known to form complexes with metals which can markedly reduce the free ion concentration of the metal and mitigate toxicity (Santore et al. 2001). Biotic Ligand Models (BLMs) for metals take account of interactions between DOC and trace metal ions, with increasing DOC concentrations typically providing a significant reduction in the bioavailability of the metal. The protective effect of increasing DOC is particularly important for copper, zinc, nickel and lead (ICMM 2007).

Therefore, advanced treatments, implemented to remove trace organic substances, may affect the discharged DOC and result in an increase in the concentration of bioavailable metals discharged in the effluent. The objective of this study was to measure and compare the concentration and form of both DOC and metals in sewage effluents subject to conventional or advanced treatment, with the aim of providing an initial indication of the effect of advanced treatment on the concentration and types of DOC and its ability to complex trace metals.

Materials and Methods

Effluents were sampled from five wastewater treatment works (WwTW) in the UK. Currently, only two UK sites operate the advanced treatments and effluents subject to both conventional and advanced treatment from these two sites were therefore included in this assessment. The other three sites all operated conventional biological treatment processes only and were selected based on their proximity to the sites employing advanced treatment. Eight effluents (two GAC treated effluents, one ozone treated effluent and five conventionally treated effluents) were sampled in total.

One hundred litres of each effluent was sampled from each site and analysed for dissolved metals, DOC, total EDTA, pH, calcium, conductivity and alkalinity, and DGT-labile metals.

Trace metal ‘availability’ was considered by both direct measurement of “available” concentrations using DGT (Davison and Zhang 1994) and by speciation modelling.

The trace metal speciation in the samples was calculated using both VisualMINTEQ (V 3.0) and WHAM7. For WHAM7 calculations it was assumed that 65% of the DOC was present as active fulvic acid, and for Visual MINTEQ calculations it was assumed that 50% of the DOC was present as active fulvic acid. The latter assumption used for Visual MINTEQ calculations about the nature of the DOC is also applied in the biotic ligand models for nickel, copper, and zinc in surface waters, although its applicability to sewage effluents is unknown. The assumption of 65% active fulvic acid is derived from experiments on UK surface waters (Bryan et al. 2002), and again its applicability to sewage effluents is unknown.

The DGT labile concentrations were calculated according to

$$C_{DGT} = C_{Dissolved} \text{ x } \left(f_{Inorganic} + \frac{f_{EDTA} \text{ x } D_{Inorganic}}{D_{EDTA}} + \frac{f_{FA} \text{ x } D_{Inorganic}}{D_{FA}} \right)$$

Where C_{DGT} and $C_{Dissolved}$ are the predicted metal concentrations measured by DGT, and the measured dissolved concentration respectively; $f_{Inorganic}$, f_{EDTA}, and f_{FA} are the fractions of inorganic metal, EDTA bound metal, and fulvic acid bound metal respectively; and $D_{Inorganic}$, D_{EDTA}, andD_{FA} are the diffusion coefficients of the inorganic metal species, the EDTA bound metal species, and the fulvic acid bound metal species, respectively.

Results and Discussion

Table 1 shows the results of the physico-chemical analysis of the effluents. The effluent samples were relatively similar in their composition in terms of the general chemistry and supporting parameters, and were neutral to slightly alkaline, with moderate levels of hardness and DOC. All of the samples contained EDTA at a concentration greater than 100 μg l^{-1}. The DOC concentration of the final effluent from WwTW A was reduced by approximately 40% by GAC treatment, although the reduction following GAC treatment at WwTW B was closer to 15%. Ozone treatment (WwTW B) had a relatively limited effect on DOC concentration (less than 5% removal).

The concentrations of dissolved cadmium and lead were below the limits of detection of the analytical technique in all of the effluent samples analysed, but concentrations of dissolved copper, nickel and zinc were detectable in all of the effluent samples. The dissolved concentrations are shown in Table 1. The metal concentrations in final effluents which had not been subject to advanced treatment showed similar dissolved metal concentrations to the effluent samples from the same sites which had been subject to advanced treatment. Any differences in concentration are likely to reflect variations in the influent metal concentration to the WwTW, rather than any effect of the GAC treatment on metal concentrations.

The stability constants (log values) for the complexes of nickel, copper, zinc, and calcium with EDTA are 18.56, 18.8, 16.5, and 10.7, respectively. EDTA is therefore very important in the speciation of the trace metals in these effluent samples due to the similar molar concentrations of EDTA and the metals. Iron (III) can also form very stable EDTA complexes, and competition from iron could reduce the degree of EDTA binding by nickel, copper and zinc, although iron (III) is very insoluble under these conditions. The speciation of EDTA is summarised in Table 2 for the sampled effluents, in terms of the percentage of the total EDTA in the form of each complex. The effect of EDTA complexation on the speciation of the individual metals is clearly important, although complexation by other ligands can also be a determining factor. In the case of the effluent samples in the present study, binding by other ligands, such as fulvic acid, is not expected to be important for nickel and zinc, although it is expected to play a role in copper speciation (but to a lesser extent than EDTA, based on the model predictions).

The DGT labile metal concentrations in the effluent samples are shown in Table 1. The diffusion coefficients of free hydrated metal ions within both water and the diffusive layer are well defined and it is therefore possible to calculate the "DGT labile" concentration of metal in the solution from the mass of metal accumulated in the receptor, the thickness of the diffusion layer, deployment duration, and the diffusion coefficient of the metal in the diffusion layer.

These concentrations represent the concentration of metal that is available to the DGT receptor in the samples and may therefore indicate the proportion of the total metal that is potentially available to exert effects on exposed organisms, or the relative lability of the different metal complexes. The remainder represents the concentration of the dissolved metal that is bound to the DOC (or other relatively stable metal complexes), or is not labile with respect to the DGT devices. The DGT labile fraction of the metal is typically believed to reflect the concentration of truly dissolved inorganic metal complexes, but may also include labile organic complexes of the metals. This fraction may be very similar to the free metal ion concentration under some conditions, particularly where other inorganic complexes such as hydroxides or carbonates do not dominate the solution chemistry of the metal.

Some studies have suggested that for some metals it is not only the free metal ion that is available for biological uptake, and that some other inorganic metal complexes can also contribute to toxicity. Several studies have identified a contribution to toxicity from Cu species other than the free cupric ion (Cu^{2+}), and species such as $CuOH^+$ and $CuCO_3$ have been identified as contributing to the toxicity of dissolved Cu (e.g. Wang et al. 2009). Metal complexes of this nature are likely to be included in the DGT labile fraction as they may dissociate rapidly when in contact with the DGT receptor.

Previous studies on EDTA complexes suggest that the EDTA complexes of nickel, copper and, zinc are not DGT labile. Studies on both nickel and copper using a different type of device which operated on the same principles (Hong et al. 2011, Li et al. 2005) have shown that the metal-EDTA complexes are not measured by the alternative DGT devices. Zinc-EDTA complexes are not labile to measurement by anodic stripping voltammetry (ASV) and this technique has been shown to give comparable results to DGT (Meylan et al. 2004). Other studies on copper using the same type of devices as were used in the present study (Tusseau-Vuillemin et al. 2003, Warnken 2008) have suggested that the metal complexes with EDTA are DGT labile, but that the amount of metal accumulated by the DGT device from these complexes is affected by their rate of diffusion across the hydrogel. Both possibilities are considered in the interpretation of the DGT results.

A comparison between dissolved and DGT labile metal concentrations in the effluent samples shows that DGT labile concentrations are lower than dissolved concentrations in all cases. This indicates that metal availability in these effluent samples is low relative to the dissolved metal levels, and is broadly consistent with the results of the chemical speciation modelling calculations. Rather higher levels of available metal, as defined by DGT analysis, were found compared to the predicted inorganic metal concentrations from speciation modelling. This could be due to some of the predicted metal complexes being labile with respect to DGT, or due to competition for binding by either EDTA or other organic ligands from other trace metals, including iron, which were not taken into account in the model calculations.

The comparisons between DGT labile and predicted inorganic metal species (using both Visual MINTEQ and WHAM7) indicate that the DGT devices are measuring other forms of metal in addition to the truly dissolved inorganic metal species. This suggests that the most appropriate interpretation of the DGT results should take account of the different metal species formed and their rates of diffusion through the hydrogel. The diffusion coefficients of the free metal ions at the deployment temperature are 4.68×10^{-6} cm^2 s^{-1}, 4.33×10^{-6} cm^2 s^{-1}, and 4.56×10^{-6} cm^2 s^{-1}, for copper, nickel, and zinc, respectively. While there is relatively little information available about the diffusion coefficients of metal-EDTA complexes, one study has reported these values for some metal complexes of EDTA (Furukawa et al. 2007). Reported diffusion coefficients of the complexes of divalent metals with EDTA were between 0.68 and 0.83 times those of the metal ions for Co, Sr, Cd, and UO_2^{2+}. On average the diffusion coefficients of the EDTA complexes were 0.76 times those of the free divalent metal ions. This information has been used to estimate diffusion coefficients of metal-EDTA complexes, from the free metal diffusion coefficients, for the principal metals of interest in this study.

Diffusion coefficients for fulvic acids have been reported previously (Zhang and Davison 2000) as 1.29 x 10^{-6} cm2 s^{-1}, although more recent work (Warnken et al. 2008) suggests that the diffusion coefficients of the metal-fulvic acid complexes may be larger in the field than they are in laboratory experiments. The diffusion coefficients of the metal-fulvic acid complexes were assumed not to be dependent upon the metal. The values of the diffusion coefficients for the different complexes used for estimating metal uptake by the DGT devices are shown in Table 3.

Estimation of DGT labile metal concentrations was performed using the speciation predictions from both Visual MINTEQ and WHAM7, and in both cases were found to be considerably higher than those measured by the DGT devices. Both speciation models gave closely comparable results for the distribution of metals between inorganic, EDTA, and fulvic acid species. Calculated DGT concentrations were close to two times higher than measured DGT concentrations in the majority of cases. As the diffusion coefficients for the inorganic metal species are well established, and fulvic acid is not expected to be an important ligand in most of the effluents this is most likely to be caused by uncertainties in the value of the diffusion coefficients for the metal-EDTA complexes.

The diffusion coefficients of the metal-EDTA complexes were therefore optimised for the prediction of the measured DGT results. This resulted in revised diffusion coefficients of the metal-EDTA complexes which were much closer to those derived for fulvic acid (Zhang and Davison 2000). The revised diffusion coefficients were 1.33 x 10^{-6} cm^2 s^{-1}, 1.90 x 10^{-6} cm^2 s^{-1}, and 1.79 x 10^{-6} cm^2 s^{-1}, for complexes of EDTA with copper, nickel, and zinc, respectively. There was still relatively poor prediction of the DGT results for zinc in the WwTW E effluent by both speciation models, and for zinc in the WwTW D effluent by Visual MINTEQ. In all of these cases the predicted DGT concentrations were considerably higher than the measured DGT concentrations. This may indicate the possible presence of larger, more slowly diffusing, metal complexes in these effluents than was considered by the calculations.

The DGT labile metal concentrations in the final effluents and those which were also subject to advanced treatments were very similar. The results suggests that there is no appreciable increase in the availability of trace metals following GAC treatment, although there may be a very slight increase in the availability of these three metals following ozone treatment, as measured by DGT.

The fraction of the dissolved concentration which is DGT labile (F_{DGT}) can be expressed as the DGT labile metal concentration divided by the dissolved metal concentration. This provides a measure of the relative availability (to the DGT devices) of the metals in the different effluents.

The advanced treatments considered in the present study have not had an effect on the available concentrations of nickel, copper, or zinc as measured by DGT. The fractions of DGT labile metal were relatively similar across all the effluents sampled, regardless of whether or not they had been subject to advanced treatments.

Summary

The results of this study indicate that free and inorganic metal forms make a relatively small contribution to the total dissolved metal concentrations in effluents. EDTA is the most important ligand for all of the metals considered in the sewage effluents. Fulvic acid binding is only expected to be important for copper (in these samples). Metal concentrations measured by DGT can be modelled assuming that all metal species are DGT labile, but the predictions are sensitive to the diffusion coefficients assumed for the metal EDTA complexes. There is a limited effect of the advanced sewage treatment processes on the availability of trace metals in the effluents. EDTA has been shown to be an important complexant in the effluents themselves, which would result in BLM calculations which are over-protective. As the effluents are diluted into the receiving waters the concentrations of both metals and EDTA will, in the majority of cases, be reduced thus reducing the degree of over protection of any BLM calculations. The receiving waters will, however, contain DOC which is able to complex dissolved metals, so there will be less dilution of DOC than there is of the EDTA and metal concentrations. This will mean that any over protection that might result from performing BLM calculations for the effluents themselves, due to the presence of EDTA which is not accounted for in the BLM calculations, will be considerably reduced at the point of compliance assessment.

Acknowledgements This work was funded by UKWIR as a technical sub-project of the UKWIR and Environment Agency Chemicals Investigation Programme (2008-2012).

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Table 2 EDTA Speciation of the Bulk Effluent Samples calculated by VisualMINTEQ (% of total metal concentration)

Sample	Ni-EDTA	Cu-EDTA	Zn-EDTA	Ca-EDTA
Tertiary Treated Effluent: WwTW A	24.7	4.5	43.7	27.2
GAC Treated Effluent: WwTW A	8.2	0.8	14.4	76.5
Tertiary Treated Effluent: WwTW B	24.4	6.2	47.0	22.3
GAC Treated Effluent: WwTW B	16.1	4.8	33.2	45.7
Ozone Treated Effluent: WwTW B	29.4	4.6	56.6	9.3
Tertiary Treated Effluent: WwTW C	15.4	8.8	40.3	35.5
Tertiary Treated Effluent: WwTW D	51.3	8.7	38.1	1.9
Tertiary Treated Effluent: WwTW E	8.4	56.9	31.5	3.1

Table 3 Diffusion Coefficients of Metals and Metal-ligand Complexes used for DGT Interpretation ($cm^2\ s^{-1}$)

Metal	Me^{2+}	Me-EDTA	Me-FA
Cu	4.68×10^{-6}	3.56×10^{-6}	1.29×10^{-6}
Ni	4.33×10^{-6}	3.29×10^{-6}	1.29×10^{-6}
Zn	4.56×10^{-6}	3.47×10^{-6}	1.29×10^{-6}

Table 1 Physico-chemical Analysis of Bulk Effluent Samples

	-	(mg l^{-1})	(mg l^{-1})	(µS cm^{-1})	(mg l^{-1} $CaCO_3$)	(µg l^{-1})	Dissolved (µg l^{-1})			DGT labile (µg l^{-1})		
Sample	**pH**	**DOC**	**Calcium**	**Conductivity**	**Alkalinity**	**EDTA**	**Copper**	**Nickel**	**Zinc**	**Copper**	**Nickel**	**Zinc**
Tertiary Treated Effluent: WwTW A	7.47	6.05	104	1010	195	208	3.12	9.05	18.7	0.39	2.50	5.59
GAC Treated Effluent: WwTW A	7.54	3.67	105	1020	105	127	1.09	7.42	14.6	0.27	2.48	5.93
Tertiary Treated Effluent: WwTW B	7.77	6.33	62.2	823	80.3	215	5.08	10.0	22.1	1.21	5.01	10.44
GAC Treated Effluent: WwTW B	7.79	5.3	60.8	822	76.3	186	4.45	9.76	22.6	0.80	4.73	9.96
Ozone Treated Effluent: WwTW B	7.93	6.11	62.6	827	75.9	176	5.07	10.2	24.0	1.60	5.29	11.19
Tertiary Treated Effluent: WwTW C	7.27	7.62	54.8	840	35.3	307	5.15	6.54	19.3	1.23	2.76	6.52
Tertiary Treated Effluent: WwTW D	8.14	6.48	105	1020	177	460	2.76	13.0	27.1	0.72	5.80	11.19
Tertiary Treated Effluent: WwTW E	8.25	6.08	102	883	202	174	23.6	2.90	22.0	7.86	1.25	5.15