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Reuse of Recovered Coagulants in Water Treatment: An Investigation on the Effect Coagulant Purity Has on Treatment Performance

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Abstract

Coagulant recovery offers many potential benefits to water treatment, by reducing chemical demand and waste production. The key obstacle to successful implementation is achieving the same levels of treatment quality and process economics as commercial coagulants.

This study has evaluated the selectivity of pressure-filtration in the role of a low-cost coagulant recovery technology from waterworks sludge. The treatment performance of the purified recovered coagulant was directly compared to fresh and raw recovered coagulants. DOC and turbidity removal by recovered coagulants was close to that of commercial coagulants, indicating that coagulant can be successfully recovered and regenerated by acidifying waterworks sludge. However, performance was less consistent, with a much narrower optimum charge neutralisation window and 10-30% worse removal performance under optimum conditions. This inferior performance was particularly evident for recovered ferric coagulants. The impact of this was confirmed by measuring THM formation potential and residual metals concentrations, showing 30-300% higher THMFPs when recovered coagulants were used.

This study confirms that pressure-filtration can be operated on an economically viable basis, in terms of mass flux and fouling. However, the selectivity currently falls short of the purity required for potable treatment, due to incomplete rejection of sludge contaminants.

Keywords

Coagulant recovery, water treatment residuals, waterworks sludge, ultrafiltration, alum recovery

1. Introduction

Coagulation is a widely used process in the treatment of surface water. Commonly, ferric and alum salts are dosed into raw water to neutralise the surface charge of contaminants and destabilise them. This allows the formation of larger floc particles and thus more effective removal of contaminants from the water. However, the sheer scale of water treatment requires vast quantities of coagulant chemicals and subsequently produces large volumes of waste sludge. The UK water treatment industry alone consumes more than 325,000 tonnes of coagulants [1] and produces more than 182,000 dry tonnes waterworks sludge each year [2] giving an annual cost of £41m and £8.1m, respectively for chemical purchase and disposal of the waste (adjusted for inflation to 2012 prices [3]). The opportunity to reduce these growing costs has driven research towards finding a viable means of recycling coagulants.

To this end, progress has been made in finding lower cost and more sustainable disposal routes for waterworks sludge [4]. However, coagulant demand shows little sign of declining, due to increasing world populations and climate change making drinking water sources more unpredictable and of poorer quality [5], [6]. Accordingly, the UK Water Industry Research body has highlighted *cost-effective recovery of metal coagulants* as a key step towards minimising chemical usage in water treatment [7]. In the context of public health and the stringent regulations required for drinking water quality, the users of any recycled coagulants must ensure their use does not lead to contaminant carryover or detriment to treatment performance. In the UK and US, the primary contaminant of concern is the addition of dissolved organic carbon (DOC) as a precursor to disinfection by-products (DBPs), as well as heavy metals and pathogens [8], [9]. A number of selective ion-exchange-based recovery technologies (particularly Donnan cation-exchange membranes) have been reported to achieve similar levels of purity to that of commercial coagulants [10], [11]. However, the materials required have been predicted to be prohibitively expensive for full-scale implementation under current economic conditions, with unit area costs for Donnan membranes more than three times greater than pressure-filtration membranes [12].

Conventional pressure-filtration processes should provide a lower cost method of selectively recovering coagulant and have already demonstrated their resilience and affordability in full-scale water and wastewater treatment processes [12]. Central to the success of pressure filtration in this role is balancing the rejection of predominantly organic contaminants and maintaining treated water quality with high yields and fluxes of coagulant metals. Previous research has gone some way towards resolving these issues but only gives a limited insight into the impact of recovered coagulant on treated water quality and has focussed only on alum coagulants [13], [14]. In this study, a spectrum of polymeric membranes was compared in terms of their readiness to permeate alum and ferric coagulants, while rejecting organic compounds and pathogens present in the acidified waterworks sludge. Coagulant treatment performance of the purest permeate was then compared with commercial coagulants and unfiltered, acidified waterworks sludge.

2. Materials and Methodology

2.1. Pressure filtration of acidified sludges

Unthickened and thickened sludges were taken from three water treatment works (WTW) in the UK, with a range of raw water characteristics and two coagulant types (Figure A.1; Table A.1). Raw water from the three treatment works was fractionated using Amberlite XAD-7HP and XAD-4 ion exchange resins (Rohm & Haas, PA, USA), providing three organic fractions of hydrophobic, transphilic and hydrophilic) using published methods [15].

The upland reservoir WTW treats peaty, acidic water containing largely hydrophobic compounds (with mean DOC composition of: 68% hydrophobic (HPO), 9% transphilic (TPI), 23% hydrophilic (HPI)) using ferric sulfate. The ferric sulfate-treated lowland reservoir water had a more hydrophilic character (37% HPO, 17% TPI, 47% HPI), high levels of alkalinity at ~140 mg/L as $CaCO_3$ [16]. The lowland river source had an intermediate organic character (48% HPO, 13% TPI, 39% HPI), more prone to variation in organic composition than the reservoir samples and treated using aluminium sulfate. Sludge pH was measured using a Jenway 3520 pH meter and a VWR 662-1761 conductivity probe. A 250 ml sample was filtered using Whatman 1.2 µm GF-C filters and dried at 105°C for 24 hours to determine dissolved solids concentration.

To fully dissolve the metals, concentrated sulfuric acid (>95%, analytical reagent grade, Sigma-Aldrich Ltd, Gillingham, UK) was added to 20 L containers of sludge to acidify to pH 2: a value reported as being sufficient to solubilise the majority of coagulant salts in the sludge [17]. The containers were manually agitated then left for one hour to equilibrate, and the process was repeated until a stable pH of 2 was obtained. The acidified sludges were left to settle for at least 24 hours before decanting the supernatant for use as the feed in ultrafiltration (UF) experiments.

A cross-flow membrane cell was fabricated from polyvinyl chloride (Model Products, Bedford, UK), based on a previously-reported design [18]. It was sealed with Viton O-rings and gaskets and had an available membrane surface area of 0.007 m^2 (channel dimensions: 1 mm high, 50 mm wide and 140 mm long). The cell was fed and pressurised from a 5 L HDPE vessel containing 2.7 L of acidified sludge by a Liquiflo 45-series magnetically-coupled variable speed gear pump (Michael Smith Engineers, Woking UK).

Various flat sheet membranes were selected on the basis of nominal molecular weight cut-offs (MWCO) and required pH and temperature tolerance (Sterlitech Corporation, Kent, WA, USA; Figure 1). Membranes were prepared by rinsing with deionised water from the feed side at ambient pressure. Membrane integrity was assessed by conducting clean water permeability and pressure hold testing at 414 kPa before and after the permeate tests.

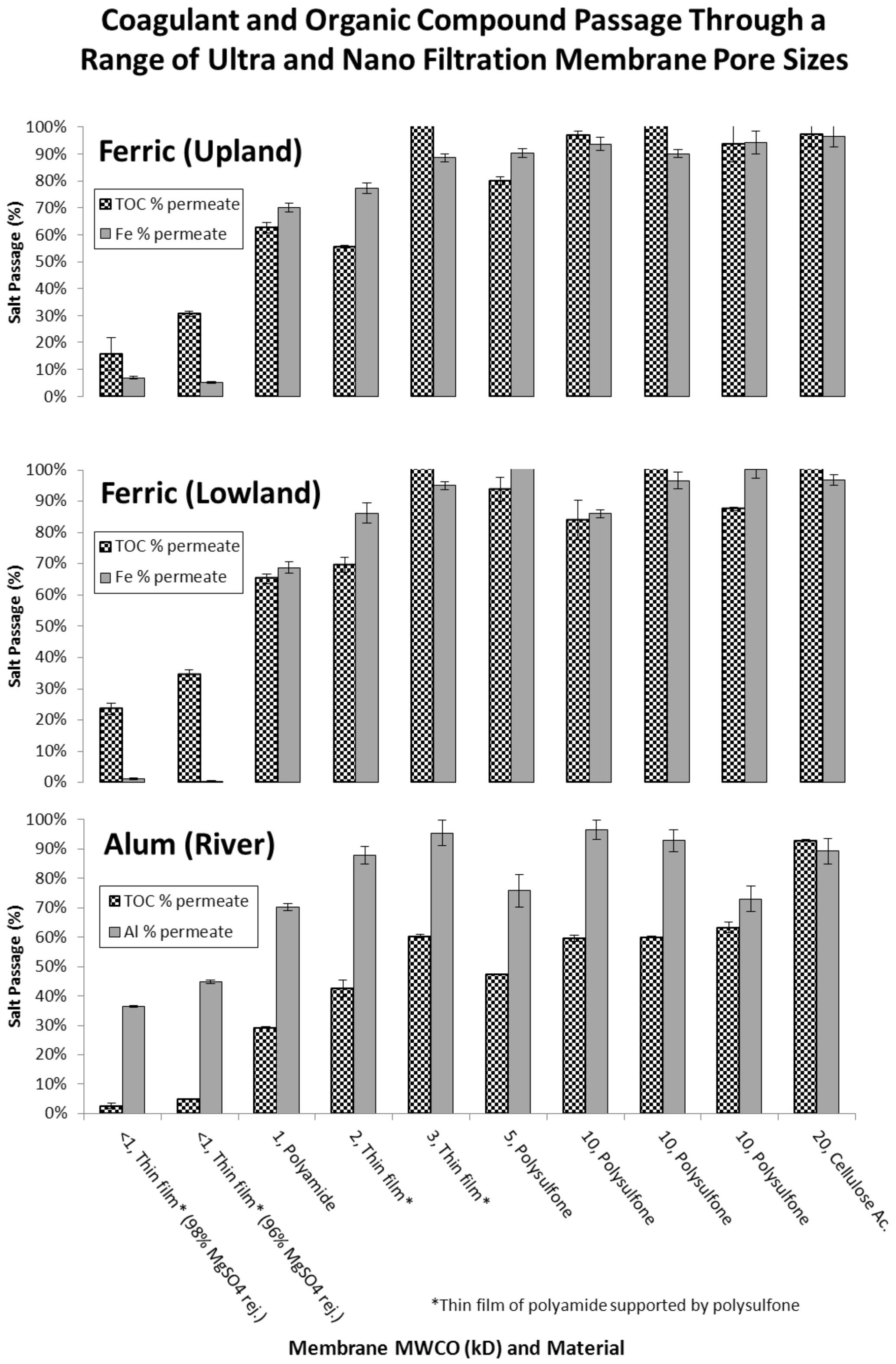

Figure 1: Coagulant and organic compound passage through a range of ultra and nano filtration membrane pore sizes

To determine the degree of separation of the coagulant metals and DOC, the acidified sludge supernatant was fed and recirculated at a cross-flow velocity of 4 m/s (Reynolds number 2350) and at transmembrane pressures (TMPs) between 276 and 414 kPa. Permeate and feed solutions were sampled in triplicate and were stored at 5°C prior to chemical analysis.

The feed and permeate samples were diluted using a 0.01M solution of analytical grade HCl (Fisher Scientific, Loughborough, UK). The diluted samples were filtered using 1.2 µm GF/C filters and analysed for DOC (as non-purgeable organic carbon in the range 0-20 mg/L) using a Shimadzu TOC-V analyser. Samples were prepared for metals analysis using a 0.01 M solution of trace metal grade nitric acid (Fisher Scientific, Loughborough, UK). Iron and aluminium samples were diluted and analysed for absorption using an A Analyst 800 atomic absorption spectrometer in the range 0-5 mg/L for Fe and 0-20 mg/L for Al (PerkinElmer, Cambridge, UK). Fresh coagulants were sampled from the same treatment works and jar test doses calculated using the metal concentrations provided by suppliers' data sheets (4% w/v as Al for alum and 13% w/v as Fe for ferric).

2.2. Jar testing using recovered coagulants

Jar tests were used to determine recovered coagulant treatment efficacy in terms of the treated water zeta potential values. Tests were conducted using a Phipps & Bird PB-700 jar tester, programmed to mix 1 L of raw water for 1 minute at 200 rpm (after which coagulant is dosed and pH is adjusted); 1.5 minutes at 200 rpm; 5 minutes at 50 rpm and 1 minute at 50 rpm. The pH was adjusted using hydrochloric acid and sodium hydroxide (0.1 M, reagent grade, Fisher Scientific, Loughborough, UK).

Treated water, extracted by syringe, was analysed for zeta potential using a Malvern Zetasizer, and for residual copper, lead, nickel, cadmium, chromium, manganese and aluminium using ICP-MS, residual iron using flame-AAS, turbidity using a Hach 2100N Turbidimeter and THM formation potential using a method [19] modified from the standard methods [20]. Treated water samples were analysed for acrylamide at Severn Trent Water's Quality Assurance laboratories, using high performance liquid chromatography., and DOC and UV_{254} absorbance were also measured.

3. Results and Discussion

3.1. Ultrafiltration

The salt passage results (Figure 1) indicate a correlation with MWCO, with values below 5kD necessitating polyamide-coated polysulfone membranes for organics rejection. At a similar MWCO, the change in membrane composition led to higher levels of permeation for alum coagulants than with uncoated polysulfone membranes but the dominant factor for permeation was MWCO. Coagulant readily permeated through membranes of nominal MWCOs of 1 kD or more, giving recoveries above 70%. In all but two cases for alum coagulant, MWCOs of 3 kD or more allowed recoveries of ~90%. MWCOs <1 kD, in the nanofiltration range, significantly reduced Al recovery and rejected almost all of the higher MW Fe salt.

For the alum sludge, DOC permeation followed a similar pattern to that of the coagulant metal but at lower levels. This is because a large amount of DOC has a higher molecular weight (MW) distribution, with the distribution peak for most NOM sources exceeding 1.5 kD [21], thereby showing the potential for separation and purification of recovered coagulant (with MWs of <700 g/mol for even the most hydrated alum or ferric sulfates). However, it should be noted that while less abundant, the lower MW organic compounds will still be able to permeate through all but the lowest membrane MWCOs.

Separation between ferric and DOC was less defined, with % permeation actually higher for DOC than Fe for many of the membranes studied. Ferric sludges from both lowland and upland sources gave consistently greater DOC permeation than for the alum samples, suggesting that differing organic character is not the cause. The noted difference may arise from differing charge density and subsequent organo-metallic complex strength and size: ferric and alum are both trivalent but the molar mass of Fe is nearly double that of Al. Differences in organo-metallic bond strength have been documented, with stability values for high-MW organic acid complexes nearly twice as high for ferric than aluminium ions: log *K* of 5.42 for Al^{3+} and 8.00 for

Fe^{3+} [22]. The combined effects of a low pH of 2 and ligand-interactions with metals, particularly ferric, would neutralise the surface charge rejection between the membrane pores and the DOC. This would account for the reduced DOC rejection from ferric sludge than would be expected from the nominal membrane MWCO, DOC rejection performance from the alum sludge, and typical raw water DOC peak size distribution. With concentration ratios between 2:1 and 50:1 of coagulant metals to DOC in the permeate, it is likely that the majority of permeating organics compounds will be chemically associated with the coagulant metals, along with lower MW, unbound organic compounds. The organic compounds that were retained by the UF membrane were hydrophobic, higher MW aromatic compounds that were less strongly bound to the permeating coagulant metals. This corresponds with an observable colour change of the recovered coagulants from dark brown to a straw-colour, before and after permeation.

The difference in alum and ferric recoveries contrasts with the results for the selective recovery of ferric and alum coagulants using Donnan dialysis (a process largely dependent on charge) where recovery rates and quality were similarly high for these trivalent metals [11]. The difference in Fe/Al-organic complex strength is less significant due to the much greater strength of the Donnan membrane sulfonic acid bonds with metals: the pK_a for sulfonic acid is several orders of magnitude greater than the carboxylic acid groups found in humic acid [23]. The separation data for alum is comparable with previous investigations using UF membranes of 10 kD MWCO [13], but the same degree of organic rejection at higher MWCO (>10 kD) could not be replicated [14]. Source waters described as “very dark in colour” suggest this may be due to higher-MW hydrophobic organic compounds that were more readily rejected by UF in the previous study.

To be viable at full-scale, coagulant recovery must balance high metal yields with DOC rejection. Of the membranes examined in this study, a cut-off of 2 kD appeared to best achieve these aims, with optimal separation providing 87% Al salt passage with 58% DOC rejection from alum sludge and 78-87% Fe salt passage with 30-44% DOC rejection from ferric sludge. This membrane MWCO was used as the basis for subsequent studies of permeate quality and the impact on treated water quality.

The overall process efficacy of the UF coagulant recovery system is a function of salt passage percentage and the volume percentage that can be recovered through the UF and acidification stages. A number of other studies have reported optimal recovery to occur between pH values of 2-4 [17]. A pH of 2 was thus selected as the target value for coagulant solubilisation, giving 86-95% solubilisation of total coagulant metal and comparable to results from previous studies [13, 24].

Percentage metal permeation by concentration was at least 80% for the 2 kD MWCO membrane, with volume recoveries of 80% consistently achieved. The overall coagulant recovery efficiency was thus ~60%. At full-scale, the shortfall in recovered coagulant would demand supplementation by fresh coagulant to maintain the correct dose into the main treatment stream. Whilst such efficiency losses and acid demand reduce the economic gains required of the process [7], a the 3:2 recovered:fresh coagulant blend would significantly reduce contaminant accumulation in the recovered coagulant. This would then help secure treated water quality in terms of DBPs and metals, which have been shown to be potential issues for more efficient coagulant recovery systems [25].

The rate of coagulant recovery was considered for sludge feeds of differing thicknesses (0.12-3.4% dry solids) and coagulant concentrations (100-2450 mg/L as M^{3+}). For each site, the thickened sludge feed permitted significantly greater coagulant metal mass fluxes (averaging up to 13 $g.M^{3+}/m^2/h$, compared to average values as low as 1 $g.M^{3+}/m^2/h$ for unthickened sludge) with flux values normalised against temperature, pressure and system hydrodynamics. The decrease in flux over time, by as much as 75%, due to fouling was more apparent for thickened sludges than for the unthickened sludge values which remained within 20% of the initial value.

For both thickened and unthickened sludges, diminishing fluxes were restored close to their original values by relaxation of the membrane, allowing surface fouling to dissolve in the acidic feed solution for approximately one hour. A linear relationship was evident between feed coagulant concentration and mass flux of permeate for feed concentrations below 1 g/L M^{3+}, giving a 12 g/m^2/h faster yield per 1g/L increase of feed concentration (Figure A.2). Thicker sludges showed a continued increase in flux with feed concentrations of 1.7 and 2.5 g/L M^{3+} but at approximately half the rate of increase (7 g/m^2/h per additional 1 g/L in the feed). This is in agreement with an earlier study that revealed gel-polarisation to be the principal controlling factor for mass flux; increased TMP had little effect on coagulant permeation under the conditions investigated [13].

Increasing solute concentration initially increases the diffusion gradient across the membrane and hence the solute flux. At higher concentrations the membrane surface becomes saturated and gel-polarisation occurs, limiting solute transport through the membrane. Operationally, this would mean that thicker sludges improve recovery efficiency, provided the use of polyacrylamide thickening polymers and their resulting monomers have no detrimental effect on recovered coagulant quality or membrane integrity. Analysis of water treated using recovered coagulant from thickened sludge showed no associated carryover of acrylamide when compared to water treated with fresh coagulant, with levels below the limit of detection in all cases (<0.02 μg/L).

The aim of measuring flux was to ascertain the suitability for larger scale operation of UF in this role. A previous study favourably compared the operating costs of UF with other coagulant management options but this was on the basis of an assumed mass flux that was 10-fold faster than that found in this work [12]. Although significantly different, the concentrated nature of the sludge stream only requires a small membrane area, making the overall operating costs quite insensitive to changes in these parameters. Therefore, the reported cost savings offered by UF remain valid. The recovery rates using UF presented in this study are comparable with the other successful membrane-based coagulant recovery technology, Donnan dialysis. For feed concentrations of 2500 and 1670 mg/L Al respectively after 24 hours of operation, Donnan dialysis recovered 10 g Al/m^2/h [11] compared to 8 g Al/m^2/h achieved using a 2 kD MWCO UF membrane. UF achieves this at a third of the unit area cost of Donnan ion exchange membranes. Donnan membranes, however, offer greater organic matter rejection than UF membranes while selectively recovering coagulant metals (Figure 1). It should be noted that because the presence of DOC is not an existing issue for industrially produced fresh coagulants, there is no direct regulation of it in coagulants themselves but only for their impact. Thus a subsequent test was conducted to determine the impact of the DOC content on coagulant performance, and thus the requirement for separation of coagulant metals from sludge DOC.

3.2. Recovered coagulant performance

It was hypothesised that when recovered coagulants are reused at correct doses and pH values for effective charge neutralisation, a portion of the carried over DOC will again be removed by the coagulant in the flocs, along with raw water DOC. If sufficiently removed, this could allow more economic, less selective recovery processes to be used without detriment to treatment quality. To test this, residual levels of DOC and turbidity were measured for fresh, unfiltered and ultrafiltered recovered coagulants for three water types: hydrophobic DOC-rich upland reservoir, hydrophilic DOC-rich lowland reservoir with high alkalinity, and lowland water from a flashy river with less stable organic content (Figure A.1).

In addition to the varying character of the raw waters, it was also considered important to appraise impacts of sludge quality on that of the recovered coagulant and so ultimate treated water quality. Differences in the effectiveness of UF in purifying recovered coagulants of different types have been discussed in terms of salt passage percentage (Figure 1). However, the solids concentration (Table A.1), which is highly variable due to differing thickening operation (between 4.5 g/L and 33.7 g/L dissolved solids in the unfiltered acidified sludge), may also have an effect on performance.

Residual turbidity after coagulation showed that in all cases optimal removal occurred when charge neutralisation was achieved with reference to particle surface charge measured as zeta charge. This occurred within zeta potentials of -5 to 0 mV (Figures A.3-A.5), where particle repulsion was minimal, allowing aggregation into stable flocs and thus effective turbidity removal. This range is in agreement with previous coagulation trials using fresh coagulants [26]. In all cases, coagulants were capable of treating water to 1 NTU or less and removed 60-70% of raw water turbidity for the river and upland reservoir waters. Turbidity removal for the lowland sample was less effective but raw water levels were already <1 NTU.

Average treated water turbidity values showed fresh coagulant to provide the lowest residual turbidity for the three water types examined, with average optimal values of 0.27-0.40 NTU (Figure 2). UF-purified recovered alum almost matched the turbidity residual of fresh coagulant (0.29 and 0.24 NTU, respectively), with unfiltered coagulant performing significantly worse with a residual of 1.0 NTU. This is perhaps due to the higher concentration of colloidal solids in the less pure alum (33.7 and 26.6 g/L dissolved solids respectively for the unfiltered and ultrafiltered recovered alum) combined with the relatively high degree of UF purification for the recovered alum with 87% Al permeate, 58% DOC rejection (Figure 1). The recovered ferric coagulants of varying purity were less effective, probably reflecting the reduced purification attained by the UF treatment (Figure 1). For both water types, the ultrafiltered recovered ferric gave turbidity residuals within 0.2 NTU of fresh coagulants. The unfiltered coagulants performed worse still but only by 0.15 NTU or less (Figure 2).

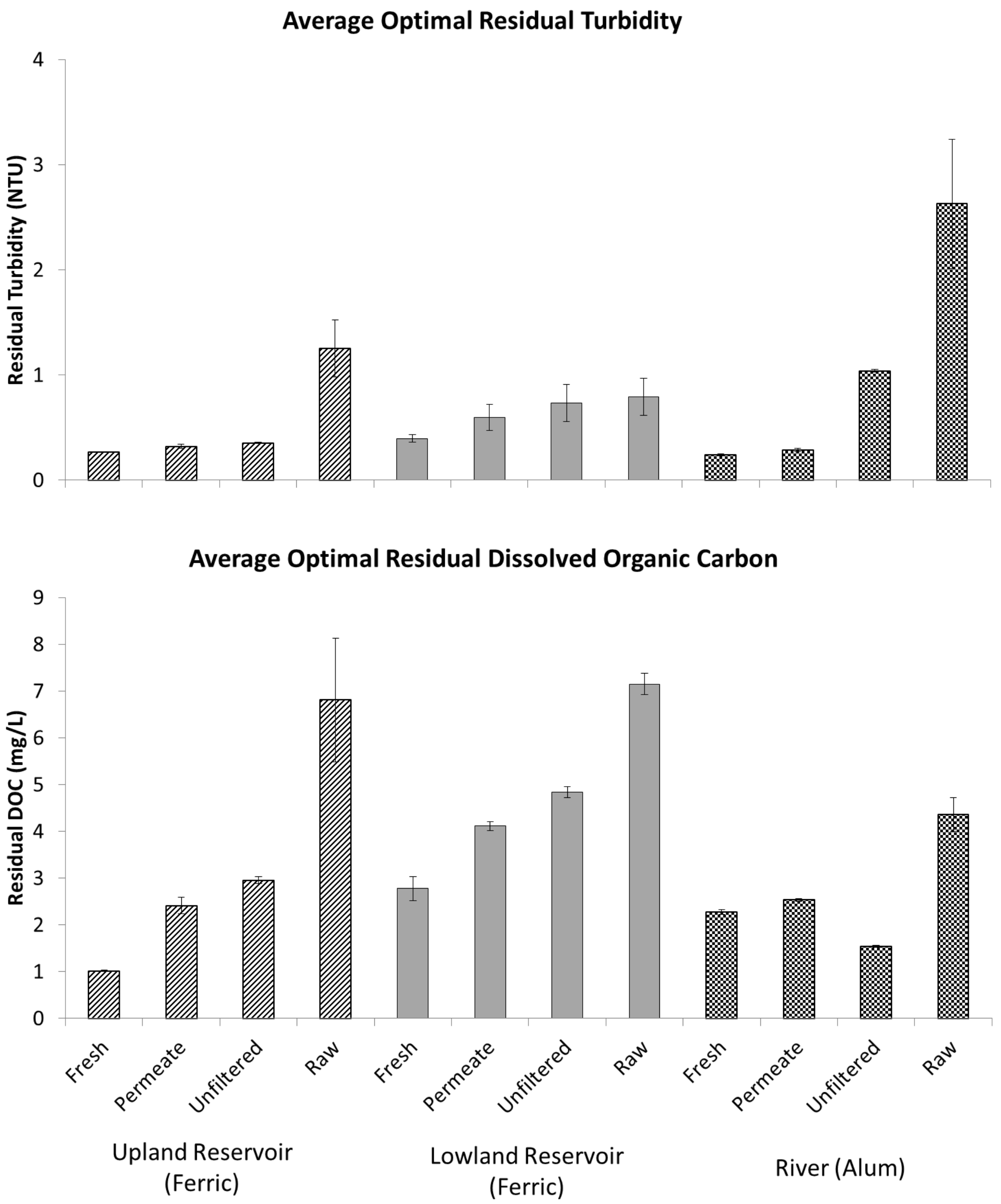

Figure 2: Residual turbidity and DOC levels for the three source waters investigated, with various coagulant types, based on the averages of the lowest three values.

Once optimised, jar tests with ferric coagulants gave a very clear trend between coagulant purity and residual DOC. Both upland and lowland waters had incrementally higher residuals for filtered and unfiltered recovered coagulants than with fresh coagulant (Figure 2; A.6-A.8). Recovered ferric was active and able to remove 30-65% of DOC from raw water, although this compared poorly with the 60-85% removal achieved with the fresh coagulants. A significant amount of carried-over DOC can be removed alongside raw water DOC by the recovered coagulant. However, DOC in the recovered coagulant appeared to impair treatment efficacy by reducing coagulant availability to neutralise the negative surface charge of raw water contaminants. This is evidenced by ~30% lower M^{3+}:carried-over DOC ratios for unfiltered coagulants (Table 1). The impact of raw water organic character also significantly influenced treatment. The hydrophobic-rich upland water (Figure A.1) permitted effective DOC removal by coagulation, with >55% removal even by the unfiltered recovered ferric. In contrast, the hydrophilic character of the lowland sample was less treatable, with the fresh ferric only achieving 55% removal and unfiltered ferric removing <30%.

The optimal DOC removal performance for the alum coagulants follows a similar trend between the fresh and ultrafiltered coagulant but, in contrast to the ferric coagulants, the lowest residual was achieved with the unfiltered recovered coagulant: the 1.5 mg/L DOC residual was almost 1 mg/L lower than of the fresh coagulant (Figure 2). The M^{3+}:DOC ratio alone does not explain this difference. It could be that the alum availability is sufficiently high for optimal charge neutralisation, even in its impure state. When differing the M^{3+}:DOC is normalised to equivalent cationic charge:DOC to take into account the different charge density of Fe and Al (based on the assumption that all coagulants are solely available in their trivalent state, following oxidation by sulfuric acid and that carried-over DOC-M^{3+} interactions are consistent between all coagulants), it suggests that the unfiltered alum is almost as available as the filtered upland ferric sample, with ratios of 0.25 and 0.29, respectively (Table 1). It is suspected that the unfiltered alum, containing a higher pre-treated DOC total, can produce a lower residual DOC than both the fresh and filtered alum due to higher dissolved solids (33.7 g/L compared to 25.9 g/L for the ultrafiltered reagent) acting as floc nucleation sites when they form their hydroxide coagulation products.

Table 1: A mass balance for DOC loadings and removals, when coagulants of differing purities are dosed.

Source, coagulant	**Coagulant state**	**Coagulant dose**			**Carried-over and dosed**	**Raw Water**	**Pre-treatment total**	**Post-treatment residual**	**Total removed**	**M^{3+} : carried over-DOC mg/L:mg/L ratio**	**M^{3+}: carried over-DOC meq:mg/L ratio**	**Total DOC removed /meq coagulant**
		Coagulation pH	**M^{3+} (mg/L)**	**meq /L ***	**DOC (mg/L)**							
Upland reservoir, ferric	Fresh	4.7	26.8	1.4	0	6.8	6.8	1.1	5.7	n/a	n/a	4.0
	Filtered	4.1	28.8	1.5	5.1	6.8	11.9	2.5	9.4	5.6	0.29	6.1
	Unfiltered	4.1	7.6	0.4	1.8	6.8	8.6	3.1	5.5	4.2	0.22	13.4
Lowland reservoir, ferric	Fresh	4.9	20	1.1	0	7.1	7.1	3.1	4.1	n/a	n/a	3.8
	Filtered	4.5	20	1.1	2.9	7.1	10.0	4.3	5.8	6.9	0.38	5.4
	Unfiltered	5.5	16	0.9	2.9	7.1	10.0	5.0	5.0	5.5	0.31	5.9
River, alum	Fresh	5.2	9.5	1.1	0	4.4	4.4	2.4	2.0	n/a	n/a	1.9
	Filtered	3.9	7.6	0.8	1.6	4.4	6.0	2.6	3.3	4.8	0.50	3.9
	Unfiltered	4.5	13.2	1.5	5.9	4.4	10.3	1.6	8.7	2.2	0.25	5.9

*Calculated assuming solely trivalent speciation of coagulant metals (following oxidation by sulfuric acid, for the recovered coagulants).

When replicate jar tests were conducted several months later with freshly sampled water from the same WTWs, using pH values and doses determined to be optimal from previous experiments, less effective DOC removal was attained for the unfiltered alum coagulant with the residual increasing from 1.5 to 3.2 mg/L (Figure 3). This may be partly due the seasonal variability of the source water (Figure A.1). Examination of the zeta potential for these replicates showed that they were on average 3 mV lower than the target value that had been achieved with the same alum dose and pH before. This highlights the increased operational complexity and unreliability of using recovered coagulants that require greater process control to treat water with constantly varying quality.

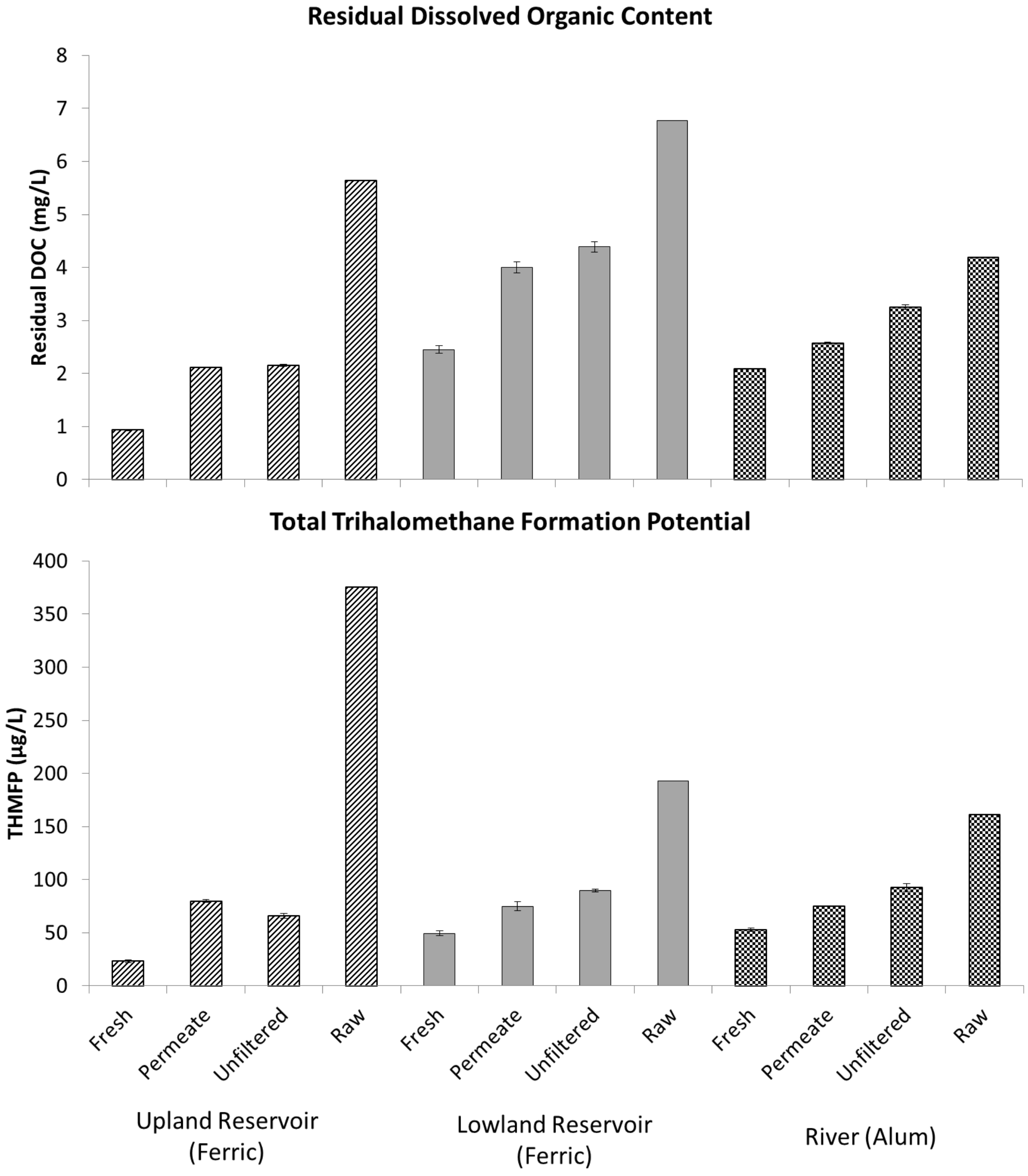

Figure 3: Trihalomethane formation potential and corresponding DOC levels for different coagulant purities and source water types.

The aim of DOC removal is to minimise the production of DBPs, of which trihalomethanes (THMs) and haloacetic acids have been of most concern to regulators and are used as indicators for total DBPs [27]. Because the source and fate of DOC are more complex when recovered coagulants are used, determining the THM formation potential (THMFP) is a critical step towards understanding the impact of recovered coagulants on this regulated water quality issue. THMFP represents the maximum possible amount of THMs DOC-containing water can produce, and is measured after adding Cl_2 in excess for a prolonged contact time to ensure THM formation approaches completion as a worst case [19]. For each water type, there was a strong correlation between residual DOC after treatment and THMFP (R^2s= 0.83-0.89). This relationship did not transcend across all of the water types due to differences in the organic compound speciation, giving a weaker correlation of R^2=0.55 when samples were grouped together. Waters containing mostly hydrophobic DOC are likely to form more THMs due to their higher reactivity [15]. In terms of reactivity with chlorine, the correlations for individual water suggests there is no significant difference in the residual organic character and its reactivity caused by the process of acidification and UF in comparison to conventionally treated water (Figure 3).

Waters treated with recovered coagulants had higher THMFPs than those treated with fresh reagent (66-93 μg/L compared to 23-53 μg/L), reflecting the higher DOC residuals (Figure 3). Water treated using ultrafiltered recovered coagulants had THMFP levels of 75-80 μg/L and would fall just within the regulatory limits of 80 and 100 μg/L for THMs set out by US and UK regulations [8], [9]. Unfiltered coagulants gave higher levels of THMs, as high as 93 μg/L and would run a risk of exceeding these regulatory limits, particularly for less effectively treated hydrophilic-rich waters. Previous investigations have never evaluated the impact recovered coagulants have on DOC removal or DBP production, although the low levels of DOC in the Donnan-purified coagulant (1 mg/L DOC per 1,600 mg/L Al) would suggest a superior performance [11].

Future legislation on DBPs will become more rigorous: in 2010 an amendment was made by the Drinking Water Inspectorate to its Water Supply Regulations, stating that English and Welsh water companies must “design, operate and maintain the disinfection process so as to keep disinfection byproducts as low as possible” [8]. Recovered coagulants will only satisfy such stringent regulatory philosophies when they can consistently match or better commercial coagulant quality. In the context of these regulations, the advantage of the relatively low recovery efficiencies discussed earlier is the necessity of supplementing recovered coagulants with fresh, thus reducing DBP-precursor loadings in the treated water relative to the recovered coagulant dose.

Another key water quality issue that coagulant recovery may impact is the concentration of regulated metals. ICP analysis has shown that recovered coagulants (both ultrafiltered and raw) increased the concentration in treated water for many of these but in most cases they remained well below the regulatory limits (Table 2). Lead and nickel regulatory limits were breached in two separate samples for ultrafiltered recovered coagulant but not in the unfiltered sludge feed. The most likely source of these loadings is from the corrosion of stainless steel and brass alloy fittings used in the crossflow cell pump and pressure gauges. This would also account for the significantly higher levels of zinc and copper in the permeate than in the raw acidified sludge (Table 3).

Manganese concentrations consistently breached the UK's regulatory limit of 50 μg/L but are less of a concern as most water treatment plant flowsheets for these types of water sources usually have specific manganese contactors downstream of coagulation-clarification-filtration, for removal of Mn and other metals. High iron residuals for the lowland ferric samples were probably caused by seasonal changes in raw water quality increasing the required ferric doses for charge neutralisation, when jar tests were repeated for metals analysis. This was evidenced by lower zeta potential values than derived from the same dose during the optimisation experiments. As UF was chosen to allow for coagulant metal recovery, rejection of these other metal contaminants cannot be expected. Unfiltered recovered coagulant, uncontaminated by corroded brass and steel, shows similar residual metal concentrations to fresh coagulants and would pass both European coagulant standards (Table 3) as well as treated water regulations (Table 2).

Table 2: Treated water residual metal concentrations

	Copper		Lead		Nickel		Cadmium		Chromium		Manganese		Aluminium		Iron	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
Upland ferric fresh	0	0	0	0	13	2	0	0	0	0	278	10	0	0	0.0	0.0
Upland ferric permeate	760	49	19	2	16	1	0	0	4	1	87	3	1	0	0.3	0.1
Upland ferric unfiltered	0	1	0	0	6	0	0	0	0	0	346	3	0	0	1.1	0.2
Lowland ferric fresh	0	0	0	0	6	0	0	0	0	0	142	9	0	0	0.1	0.1
Lowland ferric permeate	52	2	0	0	6	0	0	0	0	1	286	10	0	0	11.7	1.1
Lowland ferric unfiltered	0	0	0	0	5	0	0	0	0	1	305	10	0	0	12.2	1.2
River alum fresh	0	0	0	0	0	0	0	0	0	0	3	1	0	0	0.0	0.0
River alum permeate	102	2	4	0	23	0	0	0	3	0	90	2	2	0	0.0	0.0
River alum unfiltered	0	0	0	0	0	0	0	0	6	1	40	3	0	0	0.0	0.0
Upland ferric raw	0	-	0	-	1	-	0	-	0	-	2	-	0	-	0.1	-
Lowland ferric raw	0	-	0	-	0	-	0	-	9	-	0	-	0	-	0.0	-
River alum raw	0	-	0	-	0	-	0	-	10	-	0	-	0	-	0.0	-
DWI (2010) limits	2000		10		20		5		50		50		200		0.2	
USEPA (2009) limits	1300 (1000)		15		-		5		100		(50)		(50-200)		(0.3)	
Units	µg/L														mg/L	

Table 3: Recovered coagulant metal impurities normalised to coagulant dose, in relation to European Standards EN 888:2004 and EN 878:2004 for type 3 ferric chloride and aluminium sulfate to be used for treatment of water for human consumption [28], [29].

	Copper	Lead	Nickel	Cadmium	Chromium	Manganese	Iron	Aluminium
Maximum addition µg/g Fe	-	0.40	0.50	0.005	0.50	-	-	-
Upland ferric permeate	24.3	1.13	0.43	0.003	0.43	4	210	-
Upland ferric feed	0.1	0.21	0.09	0.003	0.07	3	221	-
Lowland ferric permeate	11.8	0.52	0.64	0.003	0.45	18	133	-
Lowland ferric feed	0.1	0.00	0.35	0.002	0.07	15	195	-
Maximum addition µg/g Al	-	0.80	1.00	0.010	1.00	-	-	-
River alum permeate	3.3	0.39	0.54	0.010	0.56	17	-	209
River alum feed	0.3	0.05	0.10	0.010	0.04	17	-	234
Units	µg/g Fe or Al						mg/L	

In Europe, the reuse of water treatment chemicals must be placed in the context of a robust regulatory environment that puts water quality and public health above all else [30]. However, water is treated on vast scales and must use relatively inexpensive methods to ensure economic viability. It was hoped that UF could undercut the costs of ion-exchange based recovery methods, while maintaining quality levels to satisfy regulations. This study shows that UF can be used to selectively recover coagulants both economically and with sufficient activity to be reused. While the recovered coagulants have approached the removal performance of fresh equivalents, performance has been less reproducible and has been undeniably inferior for many regulated parameters (Figures 2 and 3), although this is partially mitigated by UF purification.

Other studies have used adsorption, ion exchange, precipitation and filtration to further purify UF permeate [14]. Additional purification stages risk offsetting the already fragile process economics but may become viable if coagulant prices rise [1]. Sufficiently monitoring and certifying recovered quality to satisfy water treatment chemical standards would be a further operational challenge to consider. The combination of water quality regulations, operational complexity and cost all combine to make a sizeable barrier to the marginal benefits ultrafiltered recovered coagulants offer at current prices. However, this is subject to change, as historic price fluctuations have demonstrated [1]. An alternative application for recycled coagulants is for phosphorus removal in wastewater treatment which would allow the coagulant activity to be exploited without risking public health and regulatory breaches due to DOC carryover. This would allow recovered coagulant purification to be less intensive and costly, while still reducing the demand for coagulants and sludge disposal capacity [24] and thus offer a viable area for coagulant reuse.

4. Conclusions

This study has demonstrated the constraints on the efficacy of UF for coagulant recycling in potable treatment. Membrane performance in terms of flux and metal permeation for the 2 kD MWCO was in-line with expectations and would support the proposed OPEX savings suggested in a previous study. Using thickened in preference to unthickened sludge gave higher coagulant mass flux rates and would appear to be more economical. A significant percentage of DOC was rejected but levels of residual DOC and metals were far from the quality levels required by coagulant regulatory standards. Analysis of the impact these impurities had on actual treatment performance demonstrated that, in spite of the significantly higher loadings of DOC added with the recovered coagulant (in comparison to fresh coagulants), similar levels of treatment could be achieved provided they were dosed under optimum conditions. Marked treatment differences were revealed when recovered coagulants were dosed outside these optimum conditions and would represent a major operational challenge were they to be used at full-scale.

While MWCOs of <1kD have shown the potential of recovering alum with a lower level of DOC contamination, in practice this would not be viable. Due to the comparatively low value of coagulants in relation to the cost of acidification and UF operation, salt passage efficiencies of <50% would be operationally unacceptable, leaving higher-yielding, less selective UF as the only technically feasible option. When the lack of selectivity by UF for coagulant ions is viewed in the context of stringent potable regulations, for both actual treatment chemicals and treated water quality, it is clear that UF-based coagulant recovery cannot reliably meet the requirements in this role, at a practical level of recovery efficiency, despite potentially reducing net chemical costs. It would be more appropriate to reuse waterworks coagulants in wastewater treatment, where organic content is less closely regulated.

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References

1. J.L. Henderson, R.S. Raucher, S. Weicksel, J. Oxenford, F. Mangravite, Supply of Critical Drinking Water and Wastewater Treatment Chemicals - A White Paper for Understanding Recent Chemical Price Increases and Shortages, 4225, Water Research Foundation (2009) Denver, CO.

2. J.R. Pan, C. Huang, S. Lin, Re-use of fresh water sludge in cement making, Water Science and Technology, 50 (9) (2004) 183-188.

3. United Kingdom Water Industry Research, Recycling of water treatment works sludge, 99/SL/09/1, UK Water Industry Research Ltd, London, UK, 1999.

4. A.O. Babatunde, Y.Q. Zhao, Constructive approaches toward water treatment works sludge management: An international review of beneficial re-uses, Critical Reviews in Environmental Science and Technology, 37 (2) (2007) 129-164.

5. A.M. Hurst, M.J. Edwards, M. Chipps, B. Jefferson, S.A. Parsons, The impact of rainstorm events on coagulation and clarifier performance in potable water treatment, Science of the Total Environment, 321 (1-3) (2004) 219-230.

6. I. Delpla, A.-V. Jung, E. Baures, M. Clement, O. Thomas, Impacts of climate change on surface water quality in relation to drinking water production, Environment International, 35 (2009) 1225-1233.

7. United Kingdom Water Industry Research Limited, R&D Roadmap, 2007, http://www.ukwir.org/files/UKWIR/R%26D%20Roadmap%20-%2018-06-07.pdf [accessed on 22/10/2013].

8. Drinking Water Inspectorate, The Water Supply (Water Quality) Regulations 2010, DWI, London, UK, 2010.

9. United States Environmental Protection Agency, Nation Primary Drinking Water Regulations, EPA-F-816-09-0004, (2009) Washington DC, USA.

10. D. Petruzzelli, A. Volpe, N. Limoni, R. Passino, Coagulants removal and recovery from water clarifier sludge, Water Research, 34 (7) (2000) 2177-2182.

11. P. Prakash, A.K. Sengupta, Selective coagulant recovery from water treatment plant residuals using Donnan membrane process, Environmental Science and Technology, 37 (19) (2003) 4468-4474.

12. J. Keeley, P. Jarvis, S.J. Judd, An economic assessment of coagulant recovery from water treatment residuals, Desalination, 287 (2012) 132-137.

13. E.E. Lindsey, C.Tongkasame, Recovery and Re-use of Alum from water Filtration Plant Sludge by Ultrafiltration, American Institute of Chemical Engineers Symposium Series, 71 (151) (1975) 185-191.

14. H. Ulmert, E. Sarner, The ReAl process: A combined membrane and precipitation process for recovery of aluminium from waterwork sludge, Vatten, 61 (4) (2005) 273-281.

15. E.H. Goslan, D.A. Fearing, J. Banks, D. Wilson, P. Hills, A.T. Campbell, S.A. Parsons, Seasonal variations in the disinfection by-product precursor profile of a reservoir water, Journal of Water Supply: Research and Technology – AQUA, 51(8) (2002) 475-482.

16. O. Autin, J. Hart, P. Jarvis, J. MacAdam, S.A. Parsons, B. Jefferson, Comparison of UV/H_2O_2 and UV/TiO_2 for the degradation of metaldehyde: Kinetics and the impact of background organics, Water Research, 46 (17) (2012) 5655–5662.

17. J. Keeley, P. Jarvis, S.J. Judd, Coagulant recovery from water treatment residuals: a review of applicable technologies, Critical Reviews in Environmental Science and Technology, (in press).

18. D.Y. Kwon, S. Vigneswaran, A.G. Fane, R. Ben Aim, Experimental determination of critical flux in cross-flow microfiltration, Sep. Pur. Tech. 19 (2000) 169-181.

19. S.A. Parsons, B. Jefferson, E.H. Goslan, P. Jarvis, D.A. Fearing, Natural organic matter – the relationship between character and treatability, Water Science and Technology: Water Supply, 4 (5–6) (2004) 43–48.

20. American Public Health Association, Standard methods for the examination of water and wastewater, 18th Ed, (1992) Washington, DC, USA.

21. A.I. Schafer, Natural Organics Removal Using Membranes: Principles, Performance, and Cost, Technomic, (2001) Lancaster, PA.

22. P.A.W. van Hees, U.S. Lundstrom, Equilibrium models of aluminium and iron complexation with different organic acids in soil solution, Geoderma, 94 (2000) 201-221.

23. F.G. Bordwell, Bordwell pKa Table (Acidity in DMSO), http://www.chem.wisc.edu/areas/reich/pkatable/index.htm [accessed on 24/10/2013]

24. S.A. Parsons, S.J. Daniels, The use of recovered coagulants in wastewater treatment, Environmental Technology, 20 (9) (1999) 979-986.

25. G.R. Xu, Z.C. Yan, Y.C. Wang, N. Wang, Recycle of Alum recovered from water treatment sludge in chemically enhanced primary treatment, Journal of Hazardous Materials, 161 (2-3) (2009) 663-669.

26. E.L. Sharp, P. Jarvis, S.A. Parsons, B. Jefferson, The impact of zeta potential on the physical properties of ferric−NOM flocs, Environmental Science & Technology, 40 (12) (2006) 3934–3940.

27. World Health Organization, Guidelines for drinking-water quality, 4th Ed, 2011, Chapter 8.

28. EN 878:2004, Chemicals used for the treatment of water for human consumption – Aluminium sulfate, (2004), European Standard, Brussels, Belgium.

29. EN 888:2004, Chemicals used for the treatment of water for human consumption – Iron (III) chloride, (2004), European Standard, Brussels, Belgium.

30. European Union, Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption, Article 10, 1998, Brussels, Belgium.

Appendix

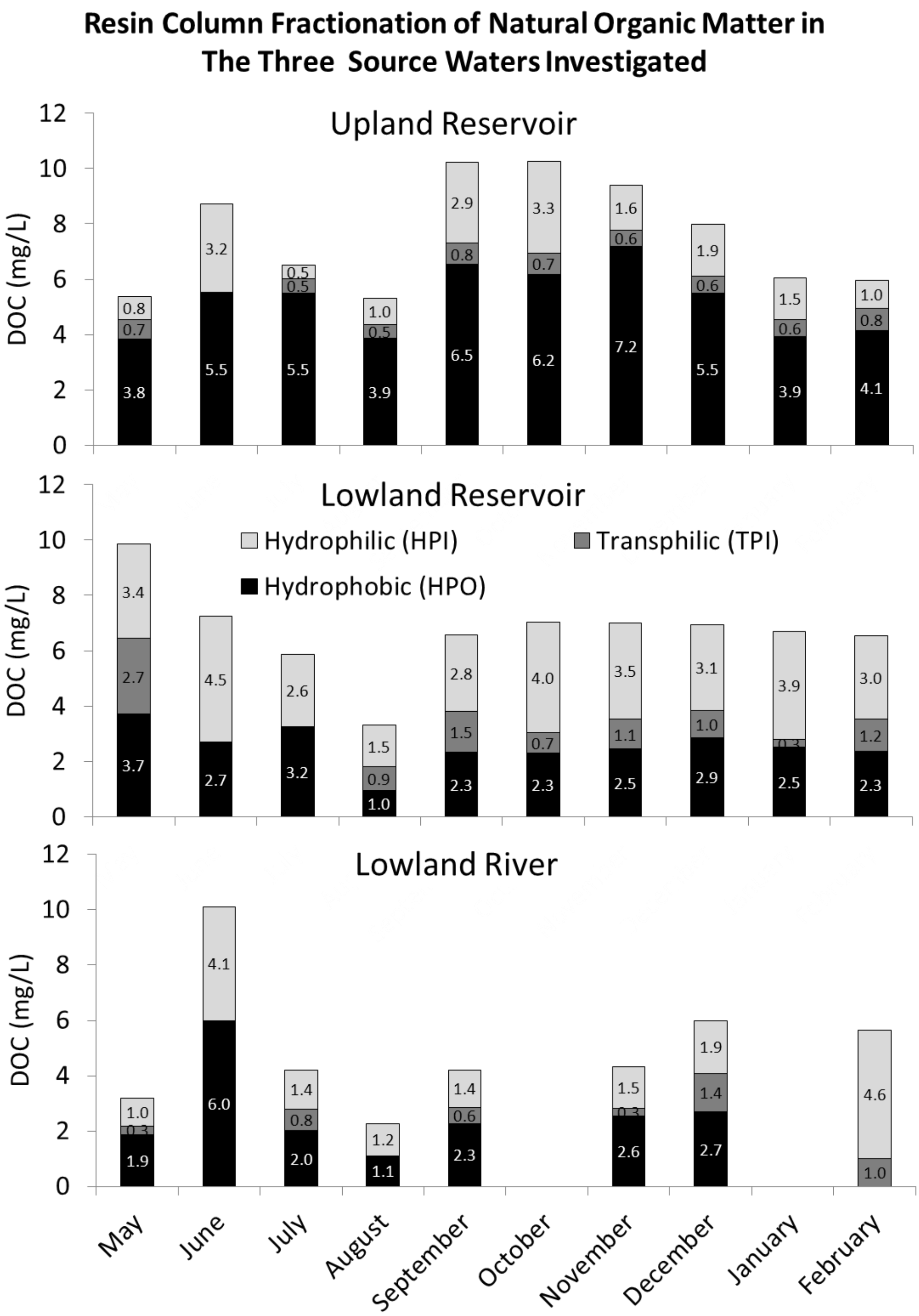

Figure A.1: Variation in raw water character for the three sites sampled and investigated.

Table A.1: Details of sludge character

Site location	Source water type	Coagulant dosed	Dissolved solids: unthickened; thickened acidified sludge (%)	Sludge pH at sample point
Derbyshire	Upland reservoir	Ferric sulfate	0.12; 0.45	4.5
Warwickshire	Lowland reservoir	Ferric sulfate	0.27; 0.55	7.3
Worcestershire	Lowland river	Aluminium sulfate	0.22; 3.4	6.5

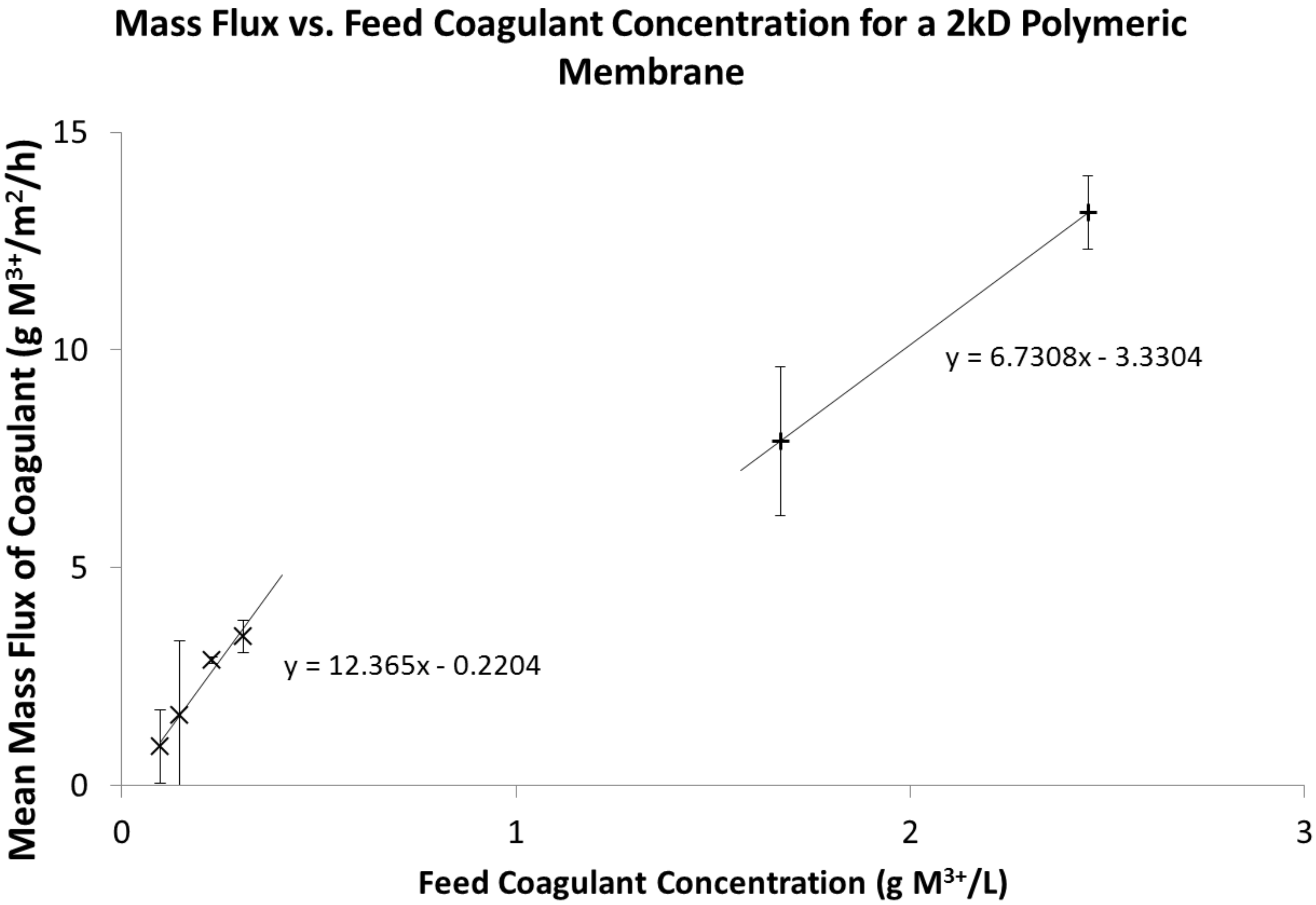

Figure A.2: The effect of coagulant feed concentration on permeate mass flux for a 2 kD MWCO polymeric membrane

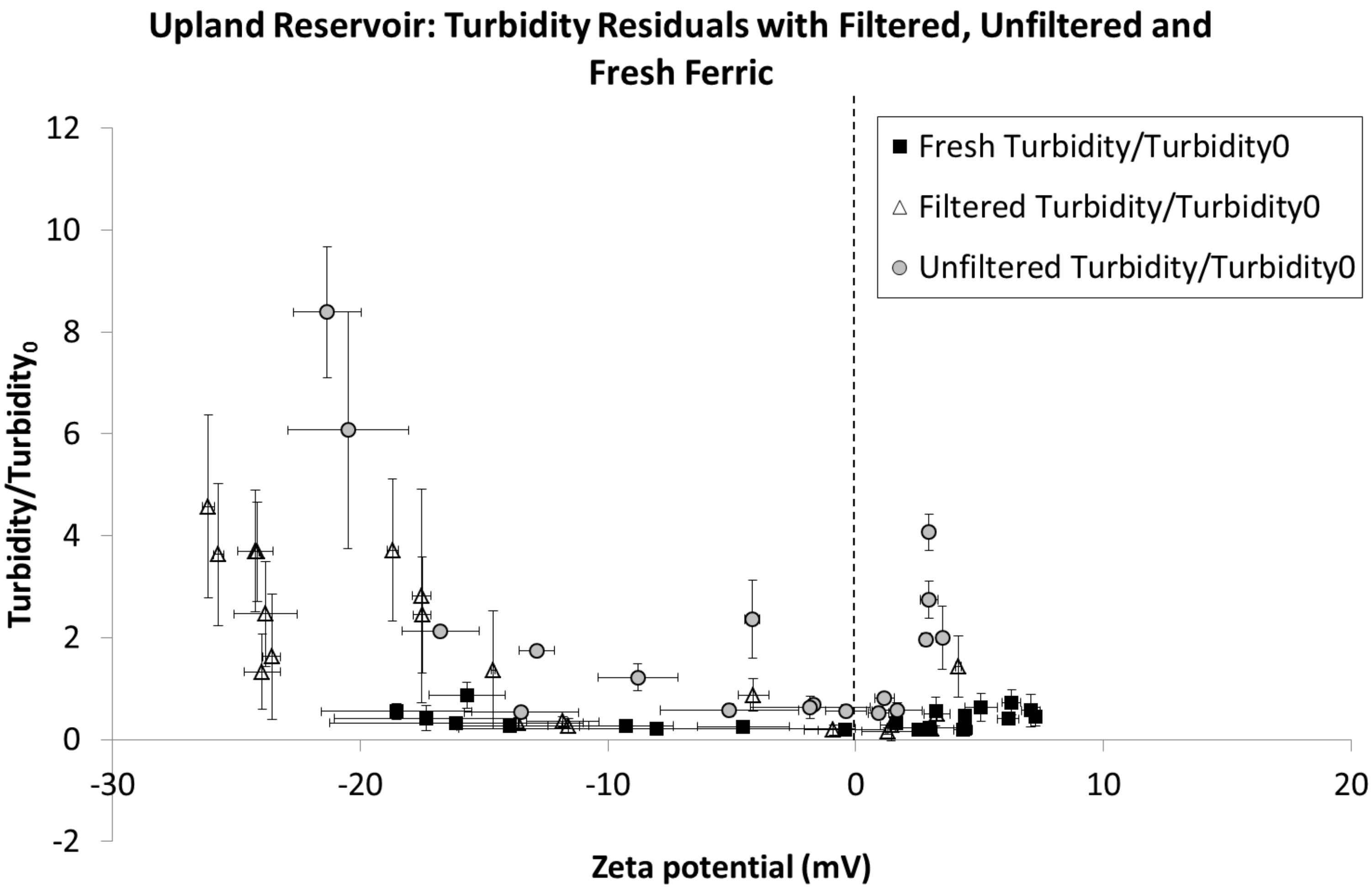

Figure A.3: Upland reservoir turbidity residuals when treated with ferric coagulants

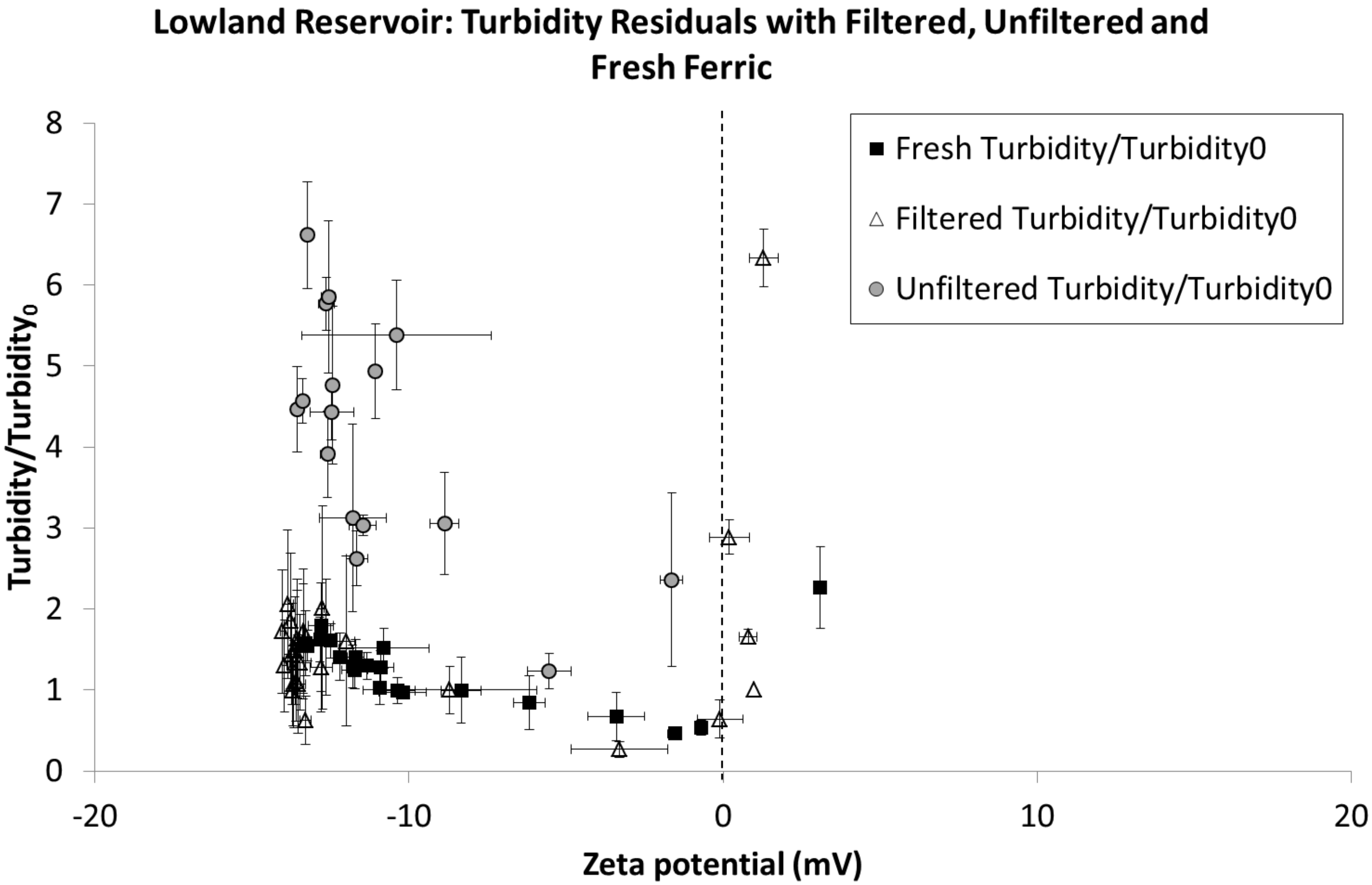

Figure A.4: Lowland reservoir turbidity residuals when treated with ferric coagulants

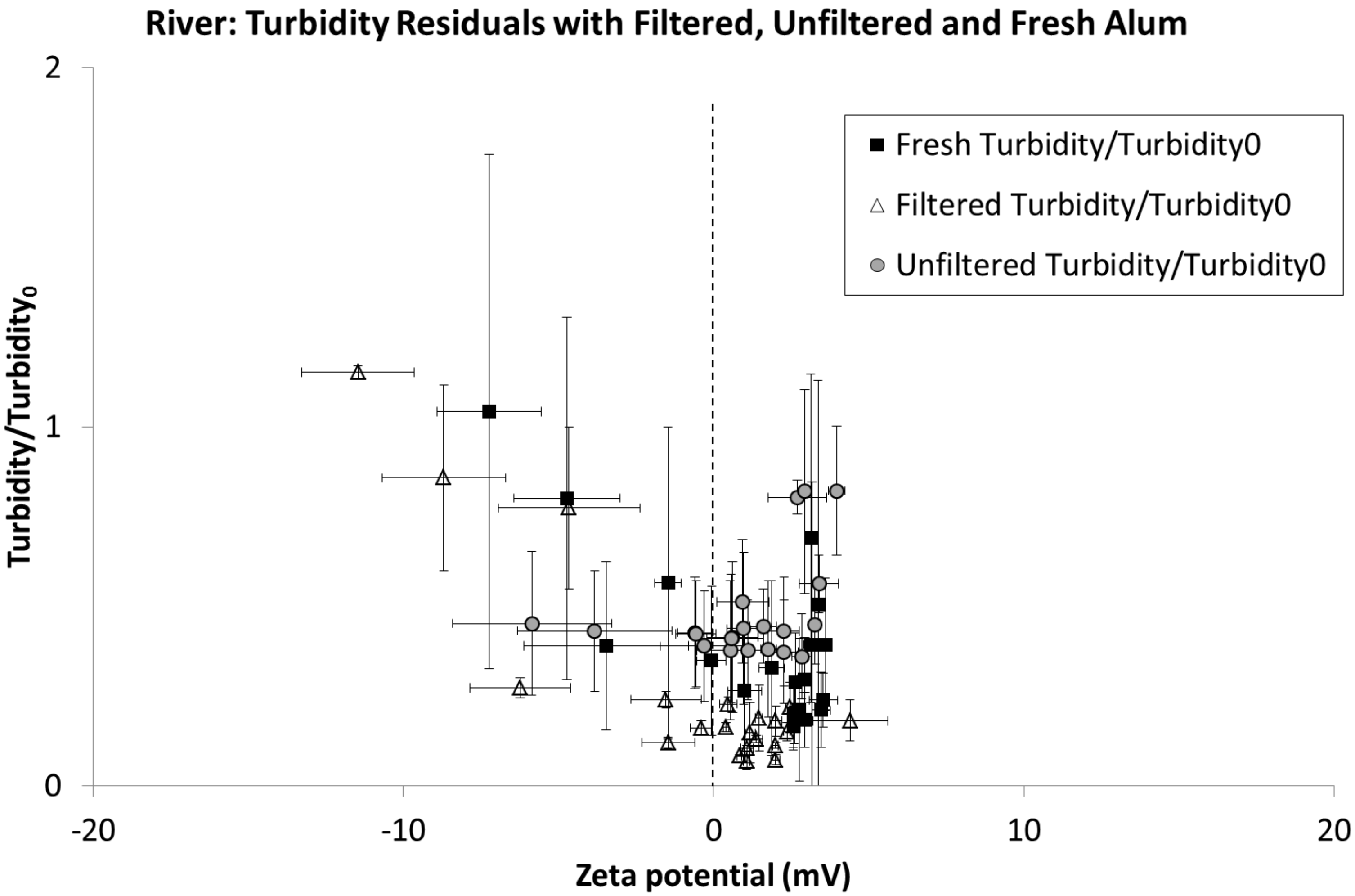

Figure A.5: River turbidity residuals when treated with alum coagulants

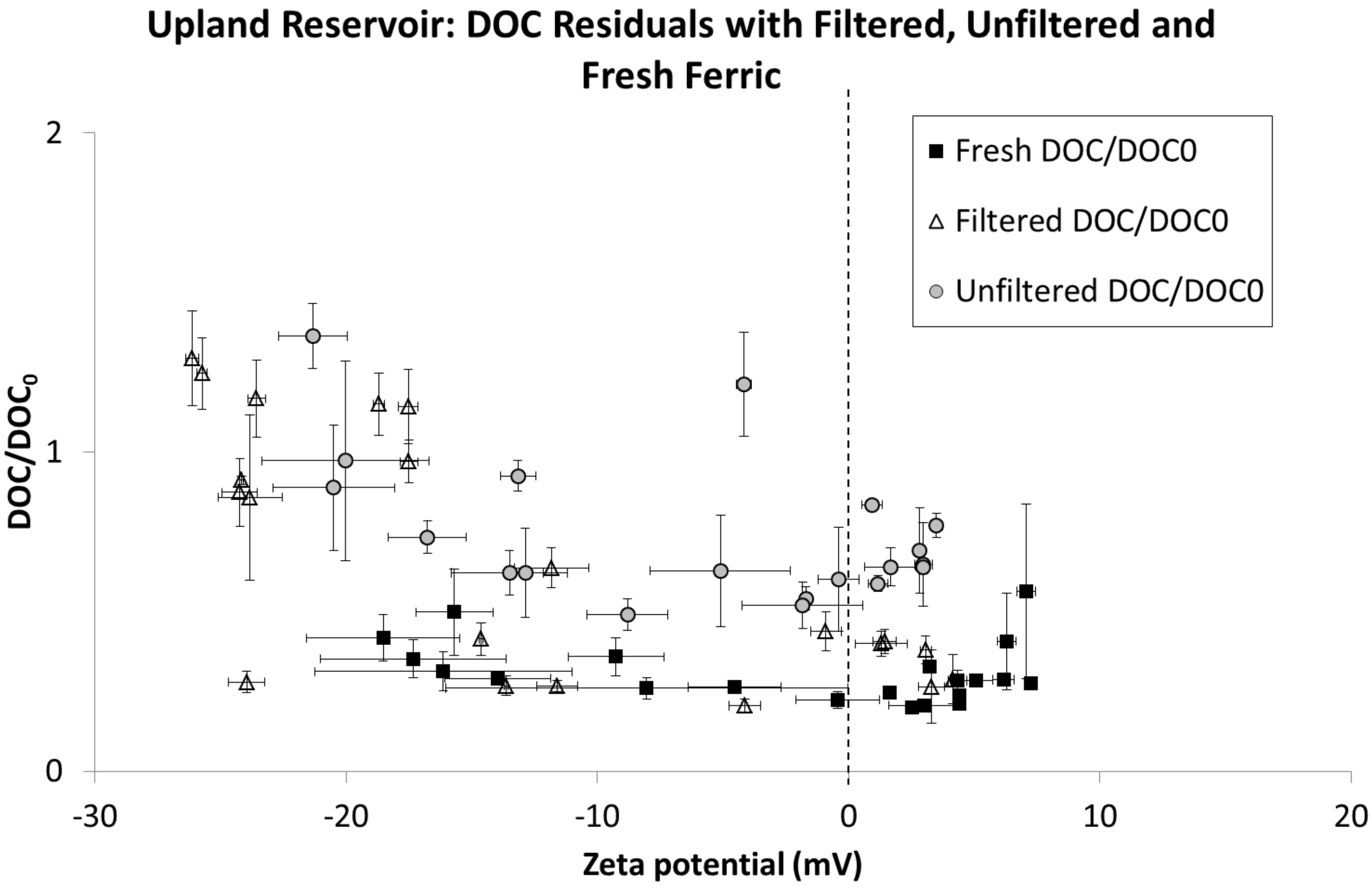

Figure A.6: Upland reservoir DOC residuals when treated with ferric coagulants

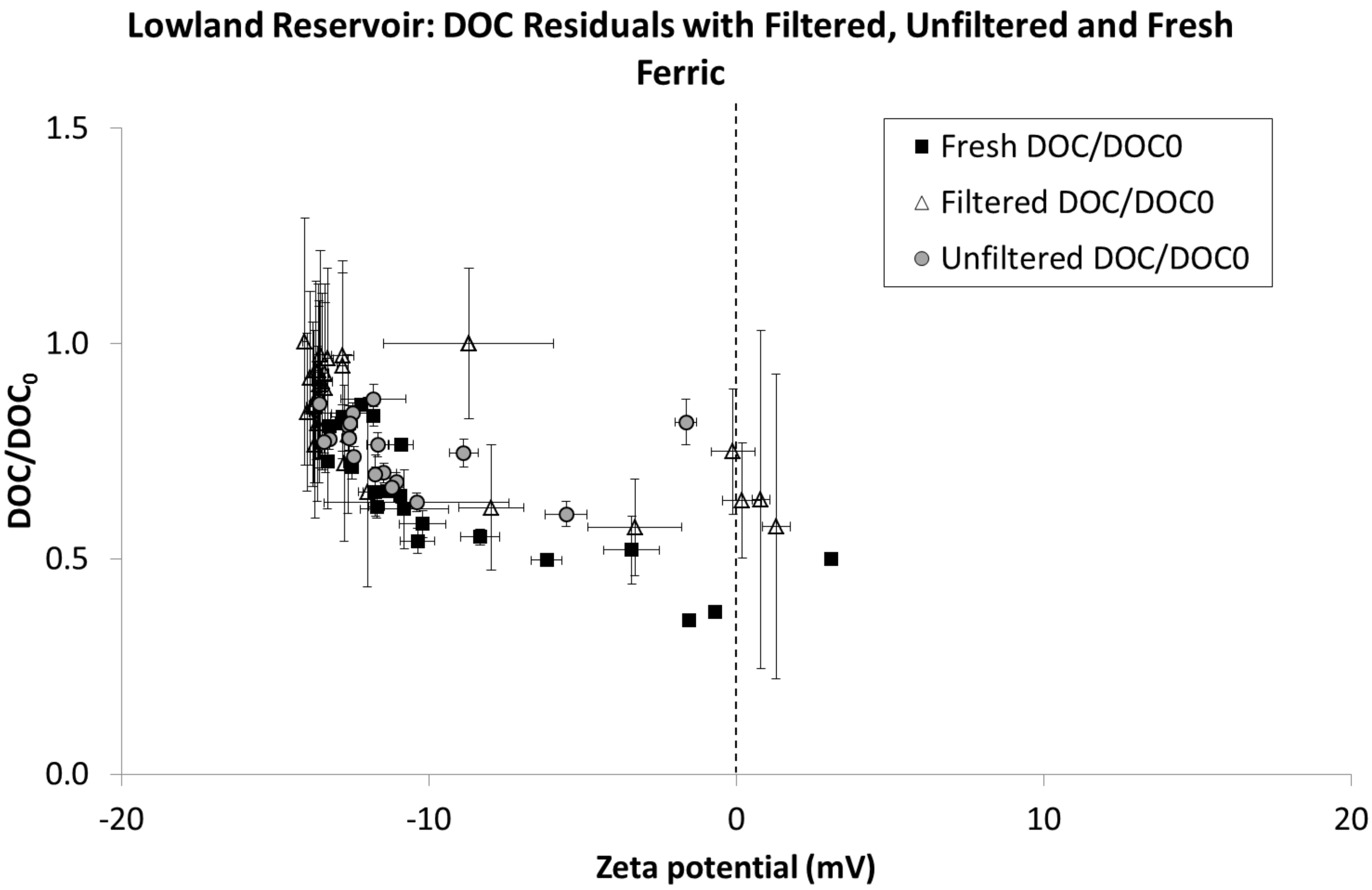

Figure A.7: Lowland reservoir DOC residuals when treated with ferric coagulants

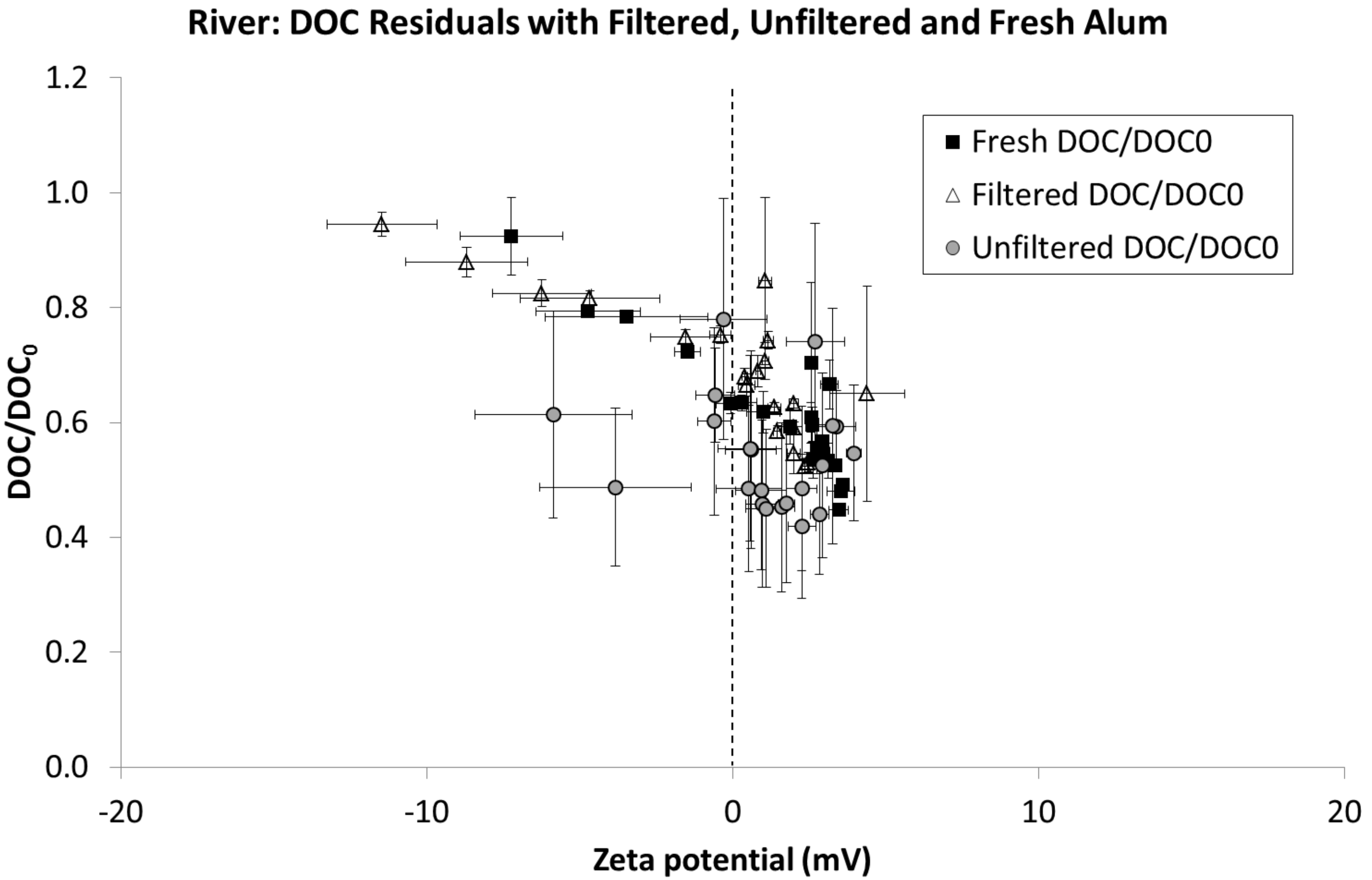

Figure A.8: River reservoir DOC residuals when treated with alum coagulants