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GETTING THE RIGHT RESULT

THE IMPORTANCE OF SAMPLE PREPARATION

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ABSTRACT

Filtration through 0.45µm membrane filters is the internationally accepted standard for analysis of dissolved parameters. However, standard methods do not generally provide further guidance on preparation of samples for analysis. This study measured colour, UV absorbance at 254nm (UV254) and dissolved organic carbon (DOC) on a range of water sources following filtration with both vacuum and syringe filtration using 0.45µm and 0.22µm mixed cellulose esters (MCE) and polyethersulphone (PES) membranes.

The filtration step was shown to affect the resulting water quality results due to a range of causes including fouling of the membrane, ineffective removal of turbidity, leaching of organics and/or "over-pressuring" (during syringe filtration). Review of this data has shown that effective filtration is critical when preparing samples for analysis to ensure accurate and consistent results. Therefore, it is recommended that filtration for preparation of samples to be analysed for true colour, filtered UV254 and DOC be undertaken with 0.45µm PES membranes using vacuum filtration.

Key Words: Organic analysis, filter membranes, vacuum filtration, syringe filtration

INTRODUCTION

Analytical water quality is determined by the measurement of a range of parameters; many of which need to be determined following filtration to remove suspended matter and obtain a result for the "dissolved" component. Filtration through 0.45µm membrane filters is the internationally accepted standard for analysis of dissolved parameters (APHA et al., 2012).

Historically filtration has been undertaken using membrane filters and applying a vacuum. Recently the use of syringe filters has been adopted, particularly when filtering small volumes, as it is more convenient, particularly when in the field. Differences obtained using vacuum versus syringe filtration were observed when undertaking analyses for UV absorbance at 254nm (UV254) and dissolved organic carbon (DOC) in a research project when analysing turbid raw water. Previous investigations undertaken when developing a suitable method to analyse true colour (Bennet and Drikas, 1993) showed that differences in colour could be attributed to ineffective filtration caused by colloidal particles passing through the membranes.

This resulted in the recommendation that the residual turbidity after membrane filtration should be less than 2% of the colour in Hazen units (HU). In ensuing years, measurement of UV254 and DOC to assess the organic character of water, both alone and in combination, has increased. These parameters are critical for optimisation of coagulation in drinking water treatment for removal of DOC to improve disinfectant stability and reduce disinfection by-product formation. The impact of filtration on these parameters was assessed by Karanfil et al. (2003) and resulted in modification to standard methodology to highlight the impact of filtration when measuring UV254 (Standard Method 5910, APHA et al. 2012). A range of filter types, including glass fibre, polycarbonate, polyethersulphone and hydrophilic polypropylene, are recommended.

However, the method also states that other filter papers that neither sorb UV-absorbing organics nor leach interfering substances may be used and that filter pore size will influence test results, particularly in raw waters. The method also states that polypropylene syringes may be used instead of vacuum filtration.

This study assessed filtration using both vacuum and syringe filtration using 0.45μm and 0.22μm mixed cellulose esters (MCE) membrane filters. The study was also extended to investigate the use of polyethersulphone (PES) membrane filters. The impact of the filtration step on the resulting colour, UV254 and DOC is discussed in this paper.

METHODS

Turbidity measurements were conducted on a 2100AN Laboratory Turbidimeter (Hach, USA) with results given in nephelometric turbidity units (NTU). Colour (456nm) and UV absorbance at 254nm (UV254) were measured following filtration, using a 5cm and 1cm quartz cell respectively, on an Evolution 60 Spectrophotometer (Thermo Scientific, USA) and reported as Hazen units (HU) and cm^{-1} respectively. Dissolved organic carbon (DOC) was measured following filtration using a Sievers 900 Total Organic Carbon Analyser (GE Analytical Instruments, USA).

Filtration was undertaken through either 47mm 0.45μm or 0.22μm membranes using vacuum filtration (VF) or by syringe filtration (SF) through 30mm disc filters of either 0.45μm or 0.22μm porosity. Filter papers utilised prior to DOC analysis were pre-rinsed with either 500mL ultrapure water (47mm membranes) or 120mL ultrapure water (30mm disc filters), unless otherwise stated. All cuvettes or vials used for analysis were also pre-rinsed with a small volume of filtered sample prior to analysis. Filter papers used were either mixed cellulose ester (MCE) by Advantec or polyethersulphone (PES) by Microscience. Ultrapure water was produced by a tandem Millipore ELIX electro-deionisation/ reverse osmosis unit and Milli-Q Gradient unit utilising Organex (trace organics removal) cartridges.

Ten litre samples were collected from each raw water source. Filtration and analysis were undertaken by the same person, with analyses of the same type on the one water completed on the same day. Each sample was individually filtered through a new filter paper five separate times to create five replicates for each analysis of each sample.

RESULTS AND DISCUSSION

Colour and UV254 Analysis

Water was collected from four different raw water sources in South Australia with varying levels of turbidity and filtration was undertaken by either VF or SF using MCE membrane filter papers with porosity 0.45μm or 0.22μm. Five replicate filtration of each sample was completed and analysed for colour and UV254. The results are summarised in Table 1.

Filtration with a syringe produced lower colour and UV254 results than vacuum filtration when using 0.45μm membrane filters for all waters except for the Myponga sample that had very low turbidity (2.1NTU).

Table 1. Average colour and UV254 after filtration through 0.45μm and 0.22μm MCE filter papers by VF and SF for different waters

	Unfiltered turbidity (NTU)	Colour (HU)*				UV254 (cm^{-1})*			
		0.45VF	0.45SF	0.22VF	0.22SF	0.45VF	0.45SF	0.22VF	0.22SF
Myponga	2.1	75 ±0.6%	75 ±0.6%	71 ±1.3%	73 ±0.0%	0.521 ±5.3%	0.514 ±0.6%	0.502 ±1.0%	0.511 ±0.5%
Morgan	16	20 ±3.5%	9 ±5.8%	6 ±7.2%	10 ±24.1%	0.111 ±2.2%	0.081 ±1.0%	0.072 ±0.8%	0.077 ±3.4%
Mt Pleasant 1	26	25 ±8.0%	11 ±13.3%	8 ±21.7%	12 ±19.8%	0.123 ±3.5%	0.088 ±4.2%	0.077 ±1.1%	0.081 ±3.5%
Mt Pleasant 2	72	65 ±5.0%	38 ±13.8%	24 ±2.3%	37 ±27.6%	0.300 ±3.3%	0.220 ±4.0%	0.179 ±0.7%	0.199 ±8.2%

(*results are the average of 5 replicates ± percent relative standard deviation)

Conversely, SF resulted in higher colour and UV254 results than VF when using 0.22µm filter papers. This difference in results was caused by the presence of suspended matter in the samples as evidenced by the turbidity present (Table 2). The higher the initial turbidity in the source water the greater the difference between VF and SF colour and UV254 results. The difference between VF and SF turbidity results, and consequently other parameters, when filtering turbid water with MCE membranes was reduced when using 0.22µm filter papers. The lowest turbidity results (<0.5NTU) were obtained when using 0.22µm VF. Karanfil et al. (2005) determined that, when filtrate turbidity was below 0.3NTU, filtration volume, filter cake formation and pre-treatment processes had no significant impact on UV254 determinations.

It was considered that the volume of water filtered may foul and change the filterability of the membrane and hence impact the resultant data, particularly when using high turbidity water sources. Using turbid water (74NTU), increasing volumes were filtered, at one time, through a single membrane and the resultant turbidity measured (Figure 1).

When using the 0.45µm membrane filter, increasing volume filtered decreased the resultant turbidity, causing differing colour and UV254 results for this sample. This effect was significantly reduced when using the 0.22µm membrane filter. When filtering large volumes of turbid water, pre-filtration using glass fibre membranes is often utilised.

This study also showed that pre-filtration resulted in greater turbidity breakthrough using MCE filters (data not shown). This was likely caused by removal of larger particulates that reduced membrane fouling.

Table 2. Average turbidity after filtration through 0.45µm and 0.22µm MCE filter papers by VF and SF for different waters

	Unfiltered turbidity (NTU)	Turbidity (filtrate)*(NTU)			
		0.45VF	0.45SF	0.22VF	0.22SF
Myponga	2.1	0.46 ±4.2%	0.36 ±11.1%	0.13 ±1.7%	0.16 ±9.2%
Morgan	16	2.7 ±4.9%	0.85 ±12.1%	0.15 ±32.7%	0.84 ±40.0%
Mt Pleasant 1	26	3.1 ±12.1%	0.81 ±33.9%	0.21 ±67.4%	0.57 ±48.3%
Mt Pleasant 2	72	8.0 ±9.2%	2.8 ±24.5%	0.57 ±6.6%	2.3 ±54.3%

(*results are the average of 5 replicates ± percent relative standard deviation)

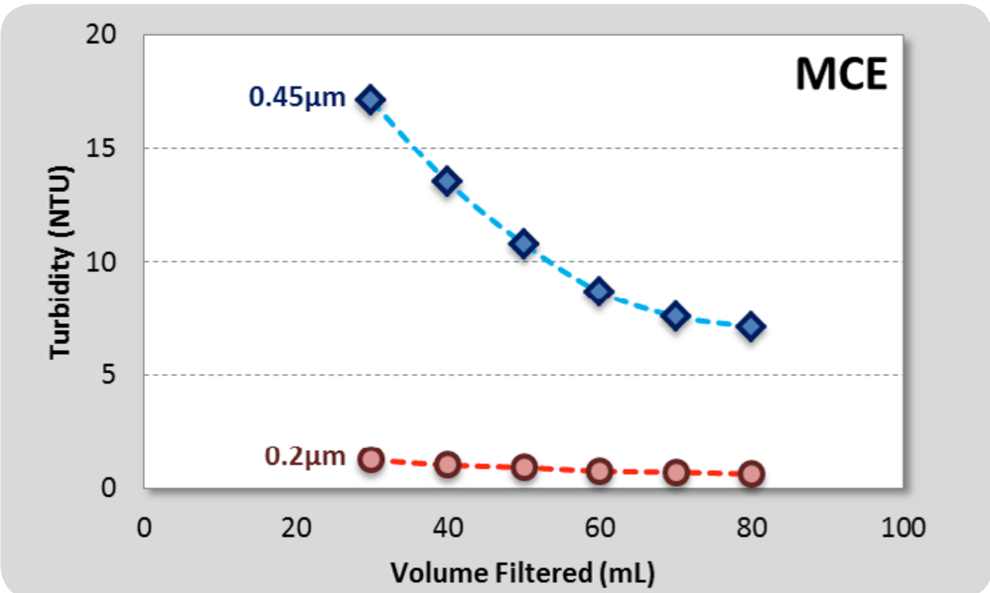

Figure 1. Impact of volume filtered on resultant turbidity using 0.45µm and 0.22µm MCE membranes (Mt Pleasant, initial turbidity 74NTU)

To minimise this impact with any filter, it is recommended that a consistent sample volume be used for all analyses and that a maximum volume of water (per unit surface area) must not be exceeded for each individual membrane filter. For 47mm membranes, 100mL is recommended.

Considering the issues identified with this particular type of filter membrane, the various filter compositions available were considered. The study was extended to compare the current mixed cellulose esters (MCE) membranes with newer generation membranes manufactured from polyethersulphone (PES). PES filters have a high internal porosity, more uniform pore shape and perform well at high flux with an excellent throughput of aqueous solutions over the entire pH range of 1–14. The low level of extractables from PES membranes also makes them suitable for environmental analysis.

The turbidity obtained after filtration using either VF or SF through both 0.45μm and 0.22μm filter papers with either MCE or PES membranes for four water sources with differing initial turbidity are summarised in Table 3. The respective and colour and UV254 data related to these samples are summarised in Tables 4 and 5.

Table 3. Average turbidity after filtration through 0.45μm and 0.22μm MCE and PES filter

	Unfiltered turbidity (NTU)	Turbidity (NTU)*							
		MCE Filters				PES filters			
		0.45VF	0.45SF	0.22VF	0.22SF	0.45VF	0.45SF	0.22VF	0.22SF
Anstey Hill	40	5.9 ±4.3%	0.44 ±67.8%	0.57 ±6.6%	1.8 ±61.8%	0.19 ±28.7%	2.5 ±0.50%	0.11 ±17.8%	0.28 ±58.5%
Morgan	21	2.9 ±0.8%	0.81 ±9.4%	0.32 ±9.0%	0.37 ±41.4%	0.14 ±14.8%	1.20 ±13.0%	0.13 ±6.7%	0.11 ±19.7%
Happy Valley	4.4	0.67 ±3.7%	0.39 ±6.1%	0.15 ±9.8%	0.18 ±14.6%	0.19 ±15.1%	1.01 ±2.6%	0.14 ±9.4%	0.12 ±11.9%
Myponga	1.60	0.21 ±9.1%	0.19 ±11.0%	0.11 ±3.2%	0.13 ±10.0%	0.20 ±8.5%	0.41 ±7.8%	0.18 ±11.4%	0.19 16.5%

(*results are the average of 5 replicates ± percent relative standard deviation)

Table 4. Average colour after filtration through 0.45μm and 0.22μm MCE and PES filter papers

	Unfiltered turbidity (NTU)	Colour (HU)*							
		MCE Filters				PES Filters			
		0.45VF	0.45SF	0.22VF	0.22SF	0.45VF	0.45SF	0.22VF	0.22SF
Anstey Hill	40	43 ±4.5%	12 ±14.8%	12 ±1.7%	23 ±38.4%	10 ±2%	25 ±15.2%	9 ±2.3%	11 ±13.5%
Morgan	21	22 ±3.3%	11 ±6.1%	8 ±1.8%	10 ±12.5%	7 ±7.4%	13 ±7.8%	7 ±3.1%	7 ±12.8%
Happy Valley	4.4	26 ±3.4%	25 ±1.8%	22 ±0.0%	23 ±2.3%	22 ±0.0%	30 ±1.9%	22 ±2.1%	22 ±2.4%
Myponga	1.60	39 ±2.3%	41 ±1.1%	38 ±0.0%	40 ±0.0%	38 ±1.2%	42 ±0.0%	38 ±0.0%	40 ±1.1%

(*results are the average of 5 replicates ± percent relative standard deviation)

Table 5. Average UV254 after filtration through 0.45μm and 0.22μm MCE and PES filter papers

	Unfiltered turbidity (NTU)	UV254 (cm^{-1})*							
		MCE Filters				PES Filters			
		0.45VF	0.45SF	0.22VF	0.22SF	0.45VF	0.45SF	0.22VF	0.22SF
Anstey Hill	40	0.178 ±2.2%	0.098 ±5.5%	0.100 ±0.7%	0.109 ±10.5%	0.086 ±0.6%	0.130 ±8.1%	0.086 ±1.0%	0.091 ±1.5%
Morgan	21	0.120 ±0.6%	0.089 ±1.8%	0.081 ±3.4%	0.082 ±0.001%	0.075 ±1.9%	0.096 ±4.0%	0.074 ±1.2%	0.079 ±1.1%
Happy Valley	4.4	0.213 ±1.0%	0.217 ±0.3%	0.201 ±0.8%	0.211 ±1.3%	0.204 ±1.0%	0.228 ±0.5%	0.201 ±1.1%	0.210 ±0.5%
Myponga	1.60	0.391 ±2.3%	0.407 ±0.1%	0.384 ±1.0%	0.405 ±0.3%	0.386 ±1.2%	0.410 ±0.1%	0.387 ±0.9%	0.405 ±0.2%

(*results are the average of 5 replicates ± percent relative standard deviation)

Turbidity was less than 0.3NTU when filtering by vacuum using 0.45μm PES membranes for all waters. Turbidity was also less than 0.3NTU and more consistent when using 0.22μm PES membranes than using MCE membranes with both VF and SF. However, when using 0.45μm SF with PES membranes, turbidity breakthrough was apparent, potentially due to 'over-pressuring', where particles that would be rejected under a constant vacuum are instead 'forced' through the membrane pore structure by application of increased pressure as filtration resistance increased. This was also observed to a lesser extent in these results and previously (Table 2) with SF using 0.22μm MCE membranes. The colour and UV254 that was analysed for these same filtered samples confirmed the trends observed with the turbidity (Tables 4 and 5). Results for colour and UV254 were consistent and reproducible following VF using both 0.45μm and 0.22μm PES membranes for all waters.

Turbidity was significantly less affected by the volume filtered under vacuum using 0.45μm PES membrane filters than using MCE membrane filters (Figure 2) even with high initial turbidity. However, it is still recommended that volumes filtered be kept below 100mL.

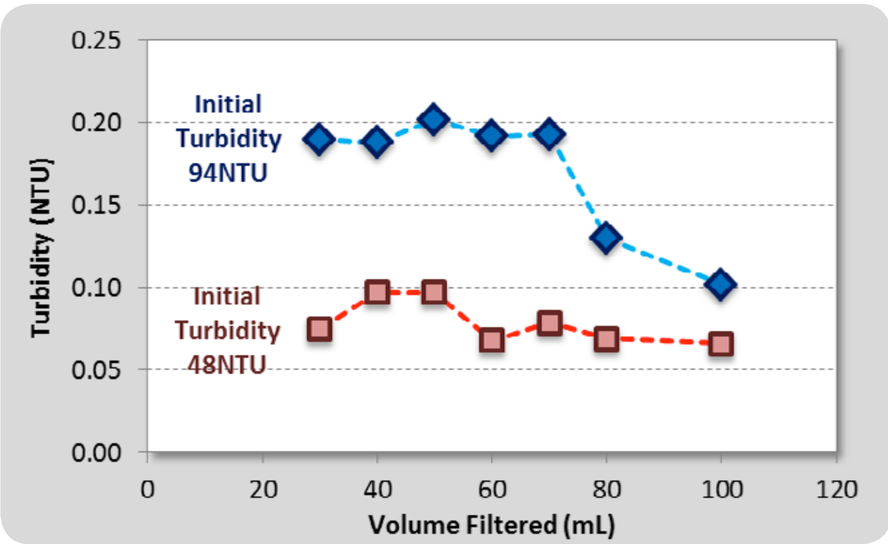

Figure 2. Impact of volume filtered through 0.45μm PES membrane on resultant turbidity

DOC Analysis

DOC analysis is, by definition, also undertaken after filtration using 0.45µm membranes. Hence, an additional key requirement for this filtration step is to ensure that the membranes used do not leach organics that contribute to DOC. DOC was measured after passing repeated 30mL aliquots of ultrapure water through each of the MCE and PES membranes. More DOC was leached from all MCE membranes than PES membranes (Table 6). As the syringe filters are smaller diameter (30mm) than the larger membranes (45mm), there is less organics leached from all the syringe filters. There was no leaching of colour or UV254 detected for either type of membrane (data not shown).

Methods for DOC analysis recommend checking filter blanks regularly but do not specify type of membrane used or extent of pre-rinsing (Standard Method 5310, APHA et al., 2012). Rinsing with ultrapure water is recommended prior to use for all membranes but the volume used could be reduced with PES membranes.

DOC was analysed after filtration through 0.45µm and 0.22µm MCE and PES filter papers for the same four waters used previously and summarised in Table 7. The associated filtered water turbidity obtained with these waters is summarised in Table 3. PES membrane filters again resulted in lower and more consistent DOC readings across all 0.45µm and 0.22µm filters than MCE membranes. However, this difference was not simply associated with turbidity breakthrough as was observed previously with colour and UV254. The major differences appeared to be associated with the use of either vacuum or syringe filtration. This difference was more apparent with the MCE filters and was attributed to the higher amount of organics leached with these filters than with the PES filters; and the larger difference in organics leached between the larger 47mm membrane than the 30mm syringe filters, even after pre-filtering with ultrapure water (Table 6).

Table 6. DOC measured after filtering 30mL ultrapure water for range of MCE and PES membranes (0.22µm VF PES membranes were not analysed)

Filter 30mL each time	MCE Filters				PES Filters		
	0.45VF	0.45SF	0.22VF	0.22SF	0.45VF	0.45SF	0.22SF
1	3.3	3.4	5.3	3.4	1.7	0.6	0.4
2	1.9	0.4	3.5	0.5	0.7	0.3	0.2
3	1.1	0.3	2.5	0.3	0.4	0.3	0.2
4	0.8	0.3	1.8	0.2	0.4	0.2	0.2
5	0.6	0.3	1.8	0.5	0.3	0.2	0.2
6	0.8	0.3	1.5	0.2	0.3	0.2	0.1
7	0.7	-	1.3	-	0.3	-	-
8	0.5	-	1.2	-	0.2	-	-
9	0.5	-	1.0	-	0.3	-	-
10	0.5	-	1.0	-	0.4	-	-
11	0.5	-	1.0	-	0.3	-	-
12	0.5	-	0.9	-	0.3	-	-
Total volume (mL)	360	180	360	180	360	180	180

Table 7. Average DOC after filtration through 0.45µm and 0.22µm MCE and PES filter papers for 4 different waters

	Unfiltered Turbidity (NTU)	DOC (mg/L)*							
		MCE Filters				PES Filters			
		0.45VF	0.45SF	0.22VF	0.22SF	0.45VF	0.45SF	0.22VF	0.22SF
Anstey Hill	40	5.2 ±4.5%	4.7 ±3.6%	5.2 ±2.7%	4.2 0.06%	4.3 ±1.9%	4.3 ±1.2%	4.2 ±3.3%	4.5 ±1.0%
Morgan	21	4.9 ±0.9%	5.0 ±2.5%	5.3 ±0.9%	5.1 ±1.6%	4.3 ±4.1%	4.2 ±0.5%	4.1 ±3.3%	4.8 ±2.7%
Happy Valley	4.4	8.4 ±4.6%	7.5 ±0.5%	8.2 ±2.1%	7.6 ±4.3%	7.3 ±2.2%	7.4 ±1.9%	7.3 ±1.6%	7.5 ±0.9%
Myponga	1.6	13.4 ±2.6%	13.5 ±1.2%	13.3 ±0.3%	13.8 ±0.9%	12.5 ±1.6%	13.3 ±0.9%	12.7 ±1.1%	13.3 ±1.3%

(*results are the average of 5 replicates ± percent relative standard deviation)

The use of PES filters resulted in more consistent results with little variation apparent between either type of filtration applied or porosity of filter membrane used. However using the Myponga source that contained higher organics, there was a measurable DOC difference between the results with the PES VF and SF for both 0.45µm and 0.22µm filters (Figure 3).

Measurable differences between PES VF and SF filtration were also observed with turbidity, colour and UV254 for all waters to some extent (Tables 3-5) and this is illustrated for turbidity with the Anstey Hill source in Figure 4.

It appears that, when using SF, turbidity and/or organic breakthrough can result, potentially due to 'over-pressuring' of the filter membrane.As these syringe filters are disposable and utilise hand filtration, it is feasible that the pressure applied can vary depending on water source, operators and even by the same operator working at different times, depending on issues such as number of samples to be analysed and time of day. For this reason, it is recommended that filtration be undertaken using vacuum filtration.

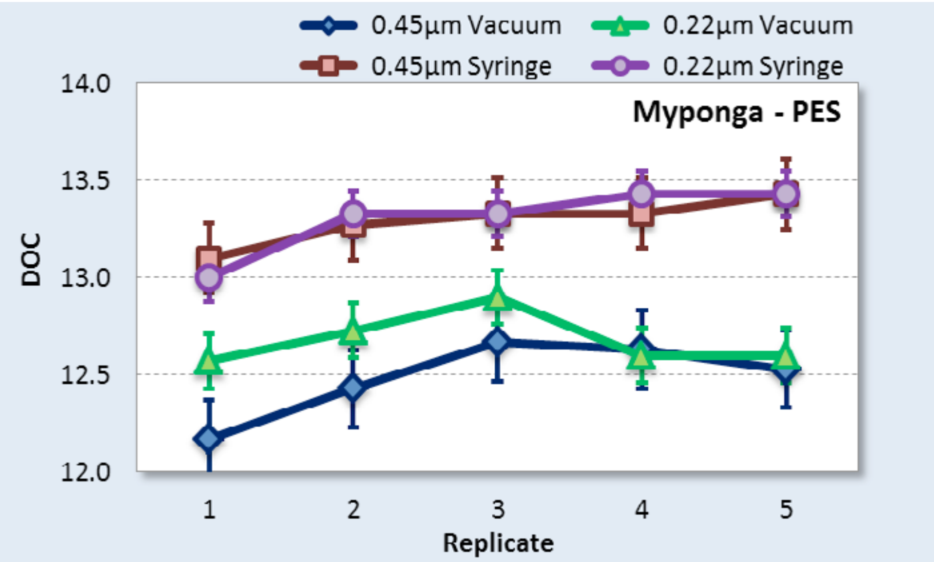

Figure 3. DOC after filtration of replicate samples through PES membranes for Myponga (initial turbidity 1.6NTU) (Error bars are one standard deviation)

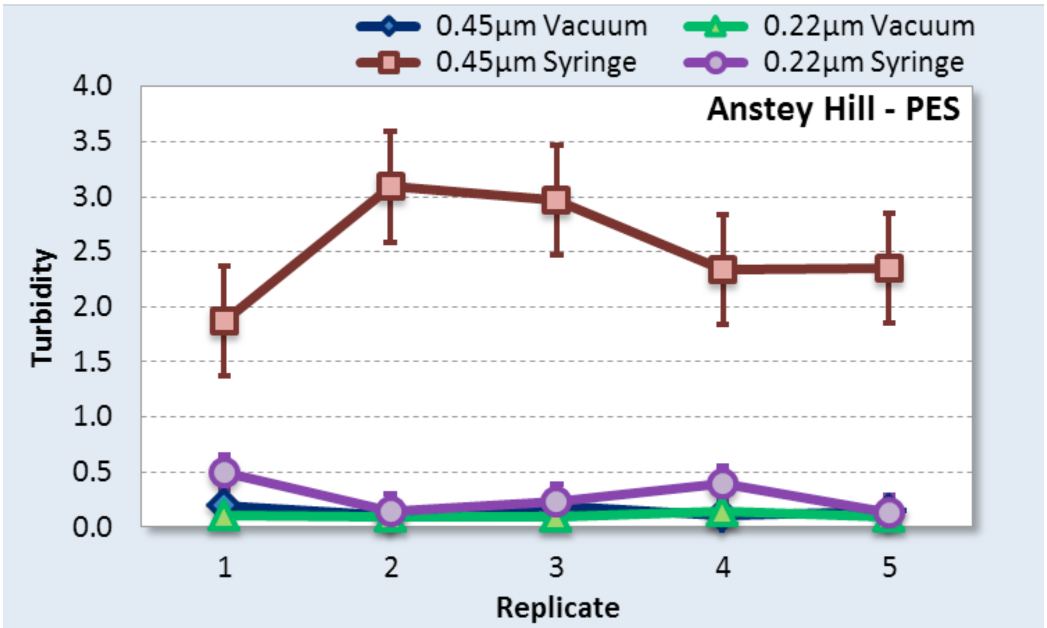

Figure 4. Turbidity after filtration of replicate samples through PES membranes for Anstey Hill (initial turbidity 40NTU) (Error bars are one standard deviation)

Conversely, this difference in DOC may also be associated with greater adsorption of DOC from the sample with the larger 47mm membrane than the 30mm membrane syringe filters.

Karanfil et al. (2003) observed uptake of some organics during filtration and recommended that the first 25mL of filtration for a 47mm prewashed PES membrane be wasted before collecting samples to minimise the filter effect on DOC measurements.

CONCLUSION

This study has indicated that it is critical to ensure effective filtration when preparing samples for dissolved component analysis to ensure accurate and consistent data is obtained. Although defined as 0.45µm porosity, different membrane materials and manufacturing process affect the efficiency of the removal of suspended matter and residual organic matter that can be leached from filter membranes. Therefore it is recommended that filtration for preparation of samples to be analysed for true colour, filtered UV absorbance and DOC be undertaken with 0.45µm PES membranes using vacuum filtration as this will minimise impact of sample turbidity and filtration conditions.

It is also recommended that the maximum sample volume filtered when using 47mm membranes should be 100mL. In addition, filters to be used to prepare samples for DOC analysis must be pre-filtered with 500mL ultrapure water to remove extractable contaminants and pre-rinsed with 25mL of sample (discarded prior to analysis) to saturate any sites that may adsorb DOC (Karanfil et al., 2003). It is also recommended that, when changing PES membrane manufacturers, testing be undertaken to assess the impact on turbidity removal, leaching and/or adsorption of organics.

While the use of 0.22µm PES membranes provided similar results, the use of 0.45µm membranes is consistent with the international standard definition for dissolved matter. This procedure can provide consistent turbidity reduction and consequently minimise any methodology-derived effect on other impacted water quality analyses for all samples analysed.

THE AUTHORS

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Rolando Fabris is a Senior Scientist with SA Water Corporation, with 20 years of water industry experience. He is a specialist in water treatment processes and characterisation of natural organic matter (NOM), but has also been involved with online monitoring, distribution systems and disinfection by-product research. Rolando has been a regular presenter in national and international water conferences since 2003 and has over 50 papers in peer-reviewed journals.

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