

# GRAPHENE MEMBRANES: IMPROVED ORGANIC REMOVAL EFFICIENCY COMPARED TO COAGULATION IN DRINKING WATER TREATMENT

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## KEYWORDS

Natural organic matter, disinfection byproducts, graphene membranes, surface water

## ABSTRACT

This study assessed a graphene oxide (GO) nanofiltration membrane for natural organic matter (NOM) removal. Four feed waters contain elevated levels of NOM were tested, from initial bench scale tests with flat sheet and spiral wound membrane to pilot scale. NOM removal improved by 25-40% compared to coagulation using aluminium sulphate.

## INTRODUCTION

### **Natural organic matter**

Natural organic matter (NOM) in surface water comprises a diverse mix of organic compounds from the decomposition of plant and animal matter. These include humic substances, fulvic acids, proteins, carbohydrates, lipids and amino acids. Surface water sourced from lakes, rivers and reservoirs supplies around 50% of the world's drinking water.

NOM affects water quality by adding colour, taste, odour and turbidity, and complicates treatment processes by increasing coagulant demand, clogging filters and membranes, and promoting microbial growth. It also leads to the formation of disinfection byproducts (DBPs). Therefore, effective NOM management is crucial for safe drinking water.

NOM levels in surface waters are influenced by environmental activities and climate change. The increased frequency of adverse natural events, such as floods, droughts and wildfires, significantly impacts NOM chemistry and concentration. These factors necessitate advanced water treatment technologies capable of managing the complex and fluctuating nature of NOM in global water sources.

### **Typical NOM removal methods**

Currently, most surface water treatment plants practise conventional coagulation processes, which include coagulation, sedimentation, rapid sand filtration and post-chlorination. The coagulation process relies on charge neutralisation of NOM, destabilising and aggregating these compounds in

water by adding coagulants such as aluminium sulphate, ferric chloride or polyaluminium chloride. Coagulated NOM and other particles form larger aggregates known as flocs, which can be easily removed through sedimentation and filtration. The coagulation process effectively reduces turbidity, enhances the efficiency of subsequent treatment processes and minimises the formation of harmful DBPs during disinfection.

However, the coagulation process has several limitations that present challenges for treatment plants. It requires the addition of chemicals, leading to the production of sludge that needs disposal. The process is pH-dependent, costly and operationally complex, necessitating careful monitoring and control of feed quality and temperature. Additionally, it may not completely remove most of organic contaminants smaller than 3000 Da MW, which potentially results in the formation of DBPs that may require further treatment.

In the past three decades, membrane technology has garnered significant attention from industries and academia for the removal of NOM from surface waters. Membrane filtration is a highly effective method for this purpose, offering several advantages. Key benefits include its ability to achieve high levels of purification by removing a wide range of contaminants, including bacteria, viruses and dissolved organic matter. Membrane processes such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) are relatively easy to automate and require less chemical usage compared to coagulation.

Polymeric membranes, despite their widespread use in surface water treatment, have significant limitations. Along with organic fouling, wide pore size distribution has restricted their applications. Fouling, caused by organic matter, microorganisms and particulates, reduces membrane efficiency and increases maintenance requirements. Historically, there has been a selectivity gap with current membrane technologies. UF membranes fail to

effectively remove a wide range of contaminants, while NF and RO membranes unnecessarily remove salts (ions). This leads to high energy consumption and difficulties in brine management. In surface water treatment, NF membranes can reject the majority of NOM from water but also remove essential salts. On the other hand, UF membranes fail to remove most nanosized NOM. Desalination through NF increases energy consumption and is often unnecessary in terms of water quality improvement and brine management.

In most surface water treatment processes, the primary goal is to remove organics rather than ions. Therefore, a membrane technology capable of removing organics within the NF range without desalination is crucial.

### Graphene membranes

In recent years, graphene oxide (GO) membranes have captured the attention of many researchers due to their vast potential in separation-related applications. Graphene oxide, a derivative of graphene, is a well-known 2D material that has revolutionised many fields of science and technology. The framework of a GO membrane is based on a robust graphitic structure functionalised with abundant hydrophilic oxygenated functional groups.

The graphitic structure of the GO nanosheets ensures chemical stability, and the plentiful oxygenated functional groups on the surface enhance the membrane's resistance to fouling. In GO membranes, well-aligned GO nanosheets are stacked on top of each other to form a continuous perm-selective film as seen in Figure 1. The interlayer spacing between adjacent nanosheets defines the membrane selectivity based on size. This unique structure provides selectivity between ions and organic compounds, allowing the passage of smaller species, such as ions, while blocking larger ones. This selective permeability makes GO membranes highly effective for various separation processes.

In this study, graphene oxide (GO) membrane treatment was assessed for NOM removal at bench scale (flat sheet and 1812 spiral wound module) in the laboratory (Figure 2) and then at pilot scale (commercial spiral wound module) at a water treatment plant (WTP). The NematiQ® GO membrane and modules are commercially available from Clean TeQ Water.

## METHODOLOGY

### Bench Scale

An initial test was completed with a flat sheet (0.0082 m<sup>2</sup>) GO membrane with a Sterlitech bench-scale cross/tangential flow membrane test cell. Feed

volume was 3 L at 2 bar and a filtration flux of 64 LMH.

A custom-built bench scale system was utilised to evaluate a 1812 spiral wound module of a graphene oxide (GO) membrane as seen in Figure 2. The unit is designed specifically to test an 1812 module in recycling mode. The membrane module contains a semi-permeable thin film of graphene oxide supported by a polyvinylidene fluoride (PVDF) substrate. The module features a 1.2 mm (46 mil) feed spacer and has a total active surface area of approximately 0.25 m<sup>2</sup>. The system includes a 50 µm mesh filter for pre-filtration, a 15 L feed tank, and a permeate tank. The retentate returns to the feed tank, while the permeate is collected in the permeate tank. During operation, the feed water is pumped from the feed tank by a centrifugal pump (P1) at a flow rate of about 4 L/min to the module. The filtration pressure is controlled using the back pressure valve.

For the experiment, the feed tank was filled with 15 L of water sample. The system was operated at 2 bar pressure. The retentate stream was recirculated back to the feed tank and the permeate was collected. Samples of permeate were collected at different recovery, for analysis.

### Operation

The NematiQ Graphene Membrane demonstration unit was operated in retentate recycled mode, as shown in Figure 3. This mode is used to determine permeate quality at various water recoveries by removing permeate out of the feed tank, and recycling the concentrate to the feed tank. By doing this, the permeate quality can be determined at various water recoveries, with the water recovery calculated using Equation 1.

$$\text{Recovery (\%)} = \frac{\text{Permeate collected (L)}}{\text{Initial feed (13L)}} \times 100$$

*Equation 1. Calculation of water recovery in retentate recycle mode.*

The water quality data was obtained for 85%, 90%, and 95% water recovery, which are potential water recoveries for a full scale operating plant. To achieve these recoveries, the required volume of permeate to be collected was calculated using Equation 1. Then the feed tank was filled with 13L of the feed solution and it was confirmed that the retentate and permeate tubes go to the feed tank and permeate tank respectively and the pump was turned on to begin operation. Once the target recovery has been achieved, the system is turned off and samples of the permeate and retentate are collected for analysis.

The system was rinsed between tests by opening the drain valve to discard the remaining solution in the

tank, refilling it with 13L of clean water, and flushing the system, with the permeate and retentate tubes going to a sink for disposal.

### **Pilot scale**

Pilot plant was operated in batch and continuous mode for 5 days over a two-week period at Barossa WTP. Testing was completed with 4040 spiral wound GO coated membrane. The pilot plant was operated at up to 90% recovery in both batch and continuous modes. Batch mode was analogous to the 1812-sized bench tests, but started with 1000 L of feed. Figure 4 shows the configuration of the pilot in continuous mode, with typical flow rates listed in Table 1.

### **Water sources**

Test waters included 3 source waters encountered in South Australia (SA), WTP inlets from Myponga, Happy Valley and Barossa Reservoirs, and a river sample from Burtundy Weir (Darling River), upstream of the junction to River Murray prior to entering SA. Myponga and Barossa Reservoirs were chosen due to persistent high (DOC) challenge (Table 1). Burtundy Weir was chosen as testing coincided with a high flow event with a large amount of organic matter present (17.2 mg/L). Water from Burtundy Weir flows into the River Murray and is a direct source to 22 WTPs treating water for customers in regional SA. Typically, DOC in the Murray River is  $\approx 5$  mg/L, spiking during high or flood level flow events (Table 1).

### **Water quality analysis**

Dissolved organic carbon (DOC), absorbance at 254 nm (UVA<sub>254</sub>) and true colour were measured to assess membrane performance for NOM removal. Specific UV absorbance (SUVA) was used for simple organic characterisation measurement and determined by (UVA<sub>254</sub>/DOC) x 100. Fractionation and molecular weight profile of the NOM was completed to assess the impact of GO membrane filtration on organic matter character.

Water quality was assessed by pH, turbidity, conductivity, alkalinity, calcium and magnesium. To assess stability regarding corrosion, Langelier Saturation Index (LSI) was calculated. Bromide was measured due to its impact on disinfection byproduct (DBP) formation and speciation.

Rapid fractionation was completed as described by (Chow et al. 2004). The apparent molecular weight of the UV absorbing compounds (at 260 nm) was determined using high performance size exclusion chromatography (HPSEC). The procedure was based on the method described by Chin et al. (1994).

Chlorine demand and DBP formation was assessed by completing a simulated distribution systems (SDS) test (3 and 10 day) with the 10 day test including a booster chlorine dose after 3 days. Settled water (pre-chlorine) from Barossa WTP and

GO membrane permeate samples were chlorinated. Settled water was used in lieu of filtered (rapid sand) water because chlorine is applied into the settled water prior to filtration. Trihalomethane (THM<sub>4</sub>), haloacetic acid (HAA<sub>9</sub>) and chloral hydrate were analysed.

## **RESULTS & DISCUSSION**

### **Bench scale**

An initial test was completed with a flat sheet GO membrane. At 75% recovery, Myponga WTP inlet water DOC was reduced from 12.7 to 3.2 mg/L (75% removal), 2.8 mg/L lower than that achieved by coagulation with aluminium sulphate at the WTP.

NOM removal with an 1812-sized spiral wound module was tested using Myponga WTP inlet, Happy Valley WTP inlet, and Burtundy Weir samples.

Feed and permeate water quality is summarised in Figure 5. DOC and UVA<sub>254</sub>nm removals were 83 and 86% respectively for the three waters (Figures 5a and b). For Myponga WTP inlet water, DOC in the GO membrane permeate was 23% or  $\approx 3.0$  mg/L lower than the long-term average ( $59.1\% \pm 5.1$ ,  $n=659$ ,  $\pm 1SD$ ) achieved with coagulation with aluminium sulphate.

Similar improvements were observed for Happy Valley WTP inlet water. Recently completed jar testing of Happy Valley WTP inlet water of similar water quality (DOC = 7.2 mg/L and UVA<sub>254</sub> = 0.200 cm<sup>-1</sup>), showed 56% DOC removal at the optimum coagulant dose (107 mg/L aluminium sulphate, pH 6.3) resulting in 3.2 mg/L DOC in the treated water.

Examination of historical WTP product DOC versus inlet DOC for Murray River water (Morgan WTP) shows that when similar high DOC water such as Burtundy Weir water has been encountered in the past, treated water DOC of 5.5 – 6.0 mg/L has been measured, which is  $\approx 3.0$  mg/L higher than that achieved with the GO membrane (Figure 6).

Conservation of pH and alkalinity (Figure 5c and 5d) was achieved, which is important for distribution system corrosion control and reduces the amount of pH control required for disinfection.

Colour removal was > 90%, with permeate colours of 2-6 HU achieved and turbidity of 0.1 and 0.2 NTU, well below the ADWG (15 HU and 5 NTU, respectively).

Pilot scale testing was completed at Barossa WTP. At the time of bench scale testing (March 2022) Barossa WTP inlet water DOC was unusually low (Figure 7a) however the long-term average since 2000 (Table 3) warranted pilot scale investigation at the WTP. DOC removal by enhanced coagulation at

Barossa WTP has been  $46\pm 8\%$   $n=158 \pm 1SD$  since January 2022 (Figure 7b) with DOC removal influenced by NOM character (SUVA) with %DOC removal increasing with SUVA (Figure 7c) which varied between 2.0 and 3.8 L/mg.m (Figure 7d).

NOM removal at pilot scale confirmed bench scale data with 85-90% and 84-89% DOC and UVA<sub>254nm</sub> removal achieved, compared with 45% and 65% DOC and UVA<sub>254nm</sub> in the WTP at the time of testing. GO membrane treatment was able to remove a greater proportion of very hydrophobic (VHA) and slightly hydrophobic (SHA) organic fractions (Figure 8a) and UV-absorbing organic matter in the  $\approx 1000 - 3000$  Dalton (Figure 8b) compared with coagulation at the WTP. A higher extent of DOC removal can reduce disinfectant demand and DBP formation. Chlorine demand (3 days, 22.5°C) of 4 permeate samples was 5-6 mg/L lower than Barossa WTP settled water (Figure 8a) but also lower than other samples representing coagulation (River Murray locations and Myponga WTP Inlet water) and MIEX (anion-exchange resin) combined with coagulation (aluminium sulphate) Figure 9a.

Laboratory SDS THM<sub>4</sub>, HAA<sub>9</sub> and chloral hydrate formation after 3 days was 324, 319 and 28.2 µg/L for WTP Settled water and 178, 98 and 4.9 µg/L for GO membrane permeate composite samples respectively, a 45-83% reduction across the 3 classes of DBPs (Figure 9b). Since the membrane does not reject bromide, the bromide to DOC ratio was higher in the GO membrane permeate compared to WTP settled water (0.21 vs. 0.05), resulting in a lesser degree of THM reduction.

Pilot scale testing confirmed bench scale conservation of pH and alkalinity (Figure 5c and 5d)

### Conclusion

Efficient removal of NOM from surface water is required ahead of chlorination, to minimise the formation of disinfection by-products. A GO membrane developed by NematIQ was tested at bench to pilot scale, and showed improved NOM rejection compared to coagulation, without sludge production.

An initial proof of concept test with flat sheet GO membrane at 75% recovery showed 75% rejection of DOC from Myponga WTP inlet (from 12.7 to 3.2 mg/L), whereas only 53% removal by possible using coagulation at the WTP (removal down to 6 mg/L). Further testing at bench scale with 1812-sized modules on three different surface water samples at up to 95% recovery resulted in similar performance (83% DOC removal, compared to 56-59% with coagulation).

Pilot scale testing on site at Barossa WTP with 4040-sized GO membrane modules reproduced the bench scale performance, with 85-90% DOC removal, significantly better than the contemporaneous 45% removal achieved by coagulation in the WTP. Permeate samples from the pilot scale testing had lower chlorine demand and produced less DBP than WTP settled water.

From bench and pilot scale testing, the following benefits of GO membrane treatment were determined:

- Organic matter removal > 80 % achieved at 90% recovery, a 25 – 40% improvement compared to coagulation
- Reduction in chlorine dose of 5 – 6 mg/L and 45 – 83% reduction in DBP formation (change in speciation)
- Conservation of calcium/magnesium (no need for post treatment stabilisation)
- Option to go from chemical dosing intensive process to technology/energy process and eliminate coagulation sludge

These findings highlight the potential for GO membranes to provide a more sustainable, effective, and operationally simpler alternative to conventional coagulation for NOM removal.

Future work may include longer-term piloting to assess energy consumption, evaluate fouling resistance over extended operation, determine sustainable maximum water recovery, and identify optimal pre-treatment requirements for consistent and reliable performance.

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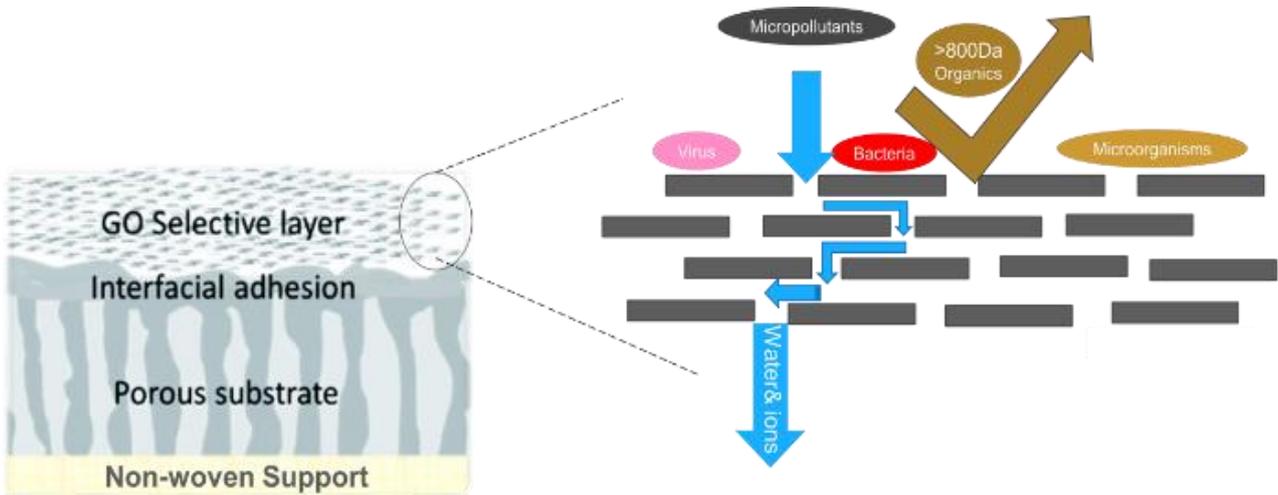


Figure 1. Schematic of the NematiQ graphene oxide membrane, which consists of a porous PVDF substrate, an interfacial adhesive layer and a selective GO layer.

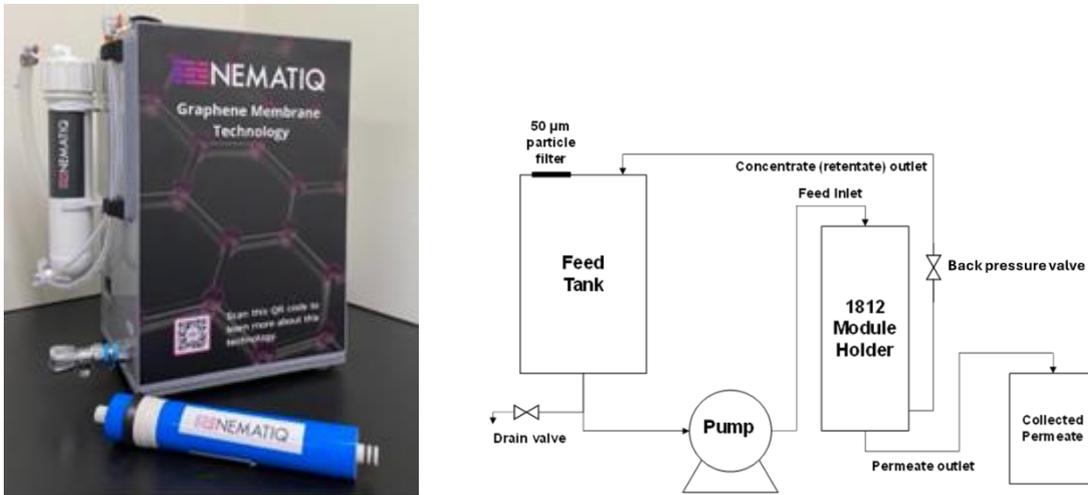


Figure 2. Photograph and P&ID of the bench scale filtration system.

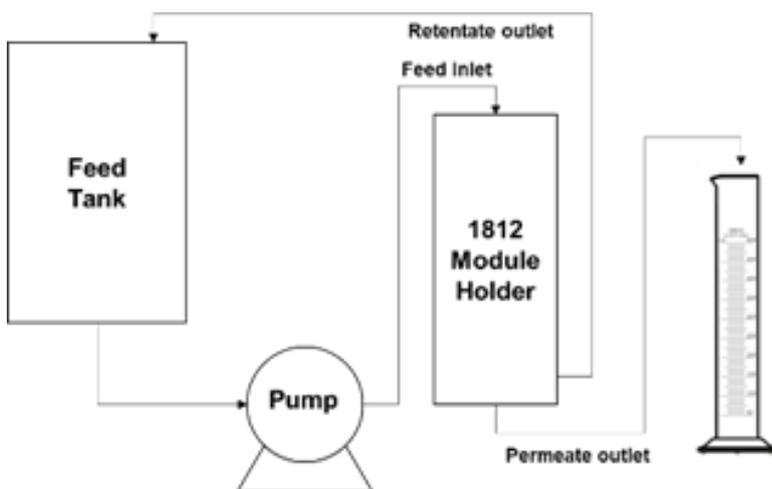


Figure 3. Diagrams showing the retentate recycled operation modes of the NematiQ Graphene Membrane demonstration unit

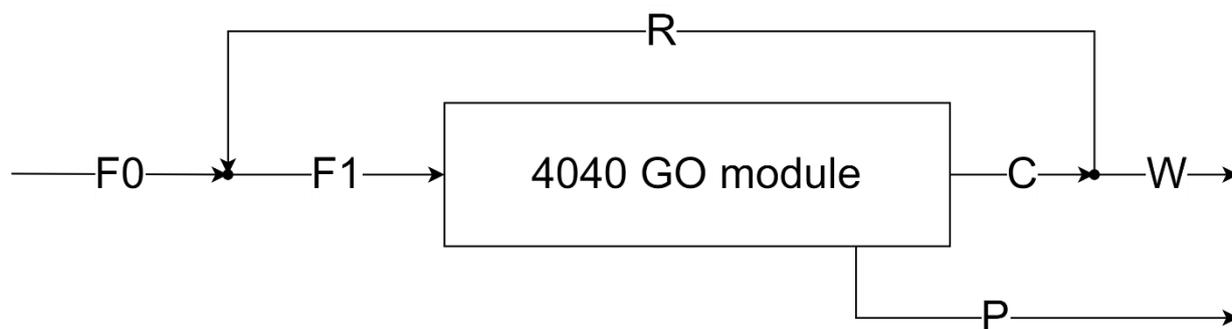


Figure 4. Pilot plant configuration; F0 = feed, F1 = feed + recycle, P = permeate, C = concentrate, W = waste, R= recycle

Table 1. Typical pilot plant flows in continuous mode (m<sup>3</sup>/h); module recovery = 10%, system recovery = 91%, recycle = 89%

Feed (F0)	Feed + Recycle (F1)	Concentrate (C)	Permeate (P)	Waste (W)	Recycle (R)
0.23	2.05	1.84	0.21	0.02	1.82

Table 2. DOC challenge and WTP treatment process for each water source

Water Source	DOC challenge	WTP Treatment Process
Myponga Reservoir	Typically, high, 12.8 ± 1.6 mg/L (n=988, ± 1 SD)	Coagulation/flocculation/dissolved air flotation/media filtration
Happy Valley Reservoir	Variable, 3.4 – 13.0 mg/L, average 7.4 ± 2.0 (1SD, n=997)	Coagulation/flocculation /sedimentation/media filtration
Burtundy Weir	Variable, 2.3 – 24.3 mg/L, average 5.6 ± 3.2 (1SD, n=1168) – at Morgan on the R.Murray	Downstream treatment includes coagulation/flocculation /sedimentation/media filtration and coagulation/flocculation/membrane/GAC
Barossa Reservoir	Typically, DOC, 9.9 ± 2.1 mg/L (n=994, ± 1 SD)	Coagulation/flocculation /sedimentation/media filtration

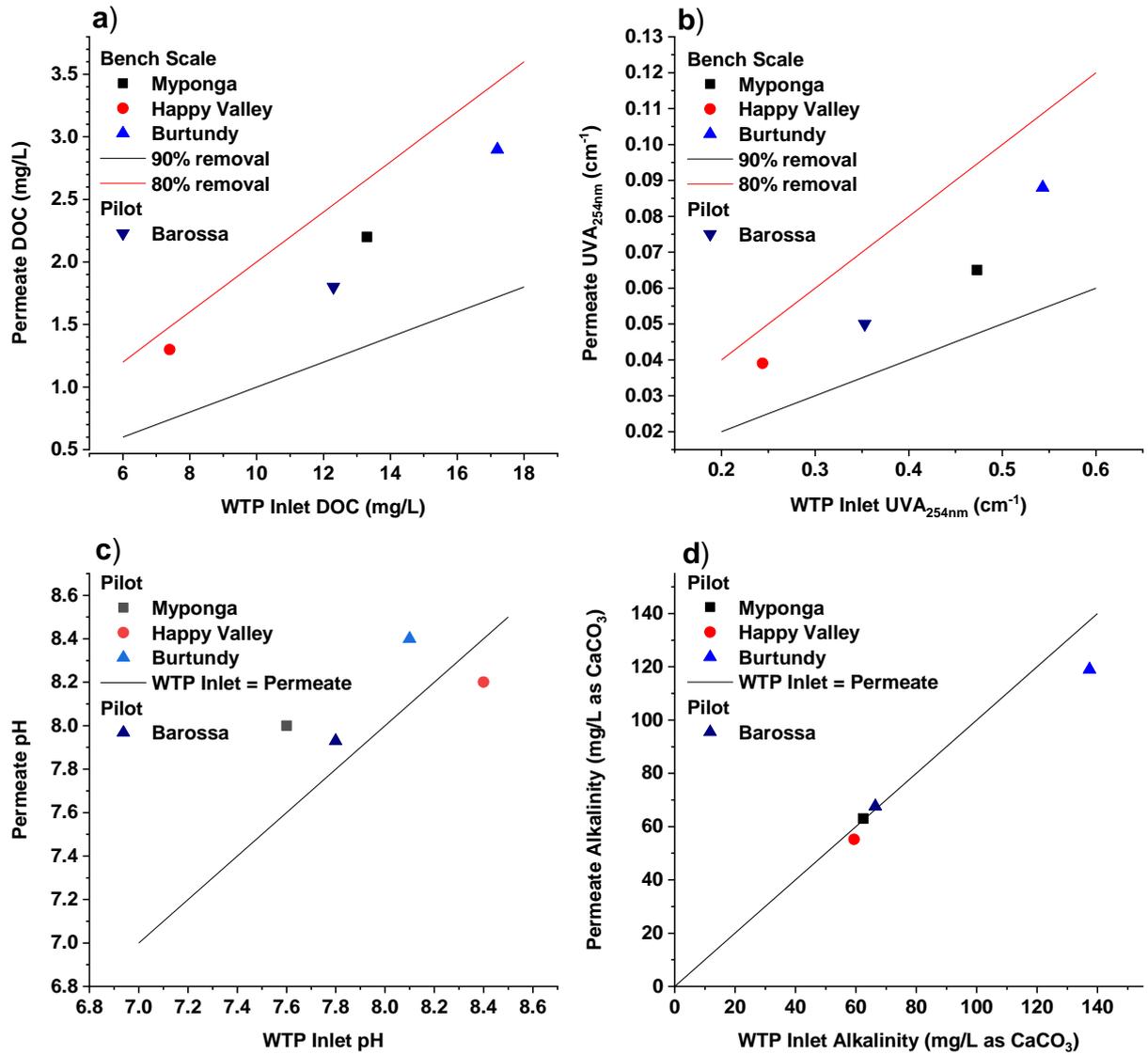


Figure 5. WTP inlet and Permeate water quality bench and pilot scale, a) DOC b) UVA<sub>254nm</sub>, c) pH and d) alkalinity

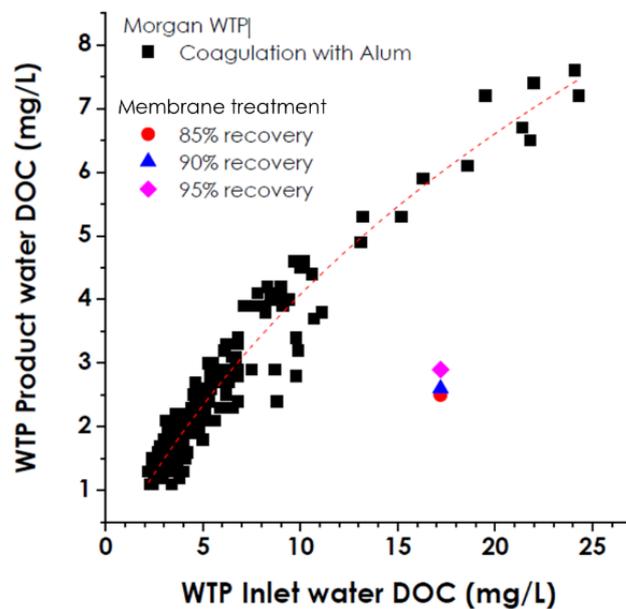


Figure 6. Morgan WTP treated water DOC as a function of inlet DOC (2016 – 2022)

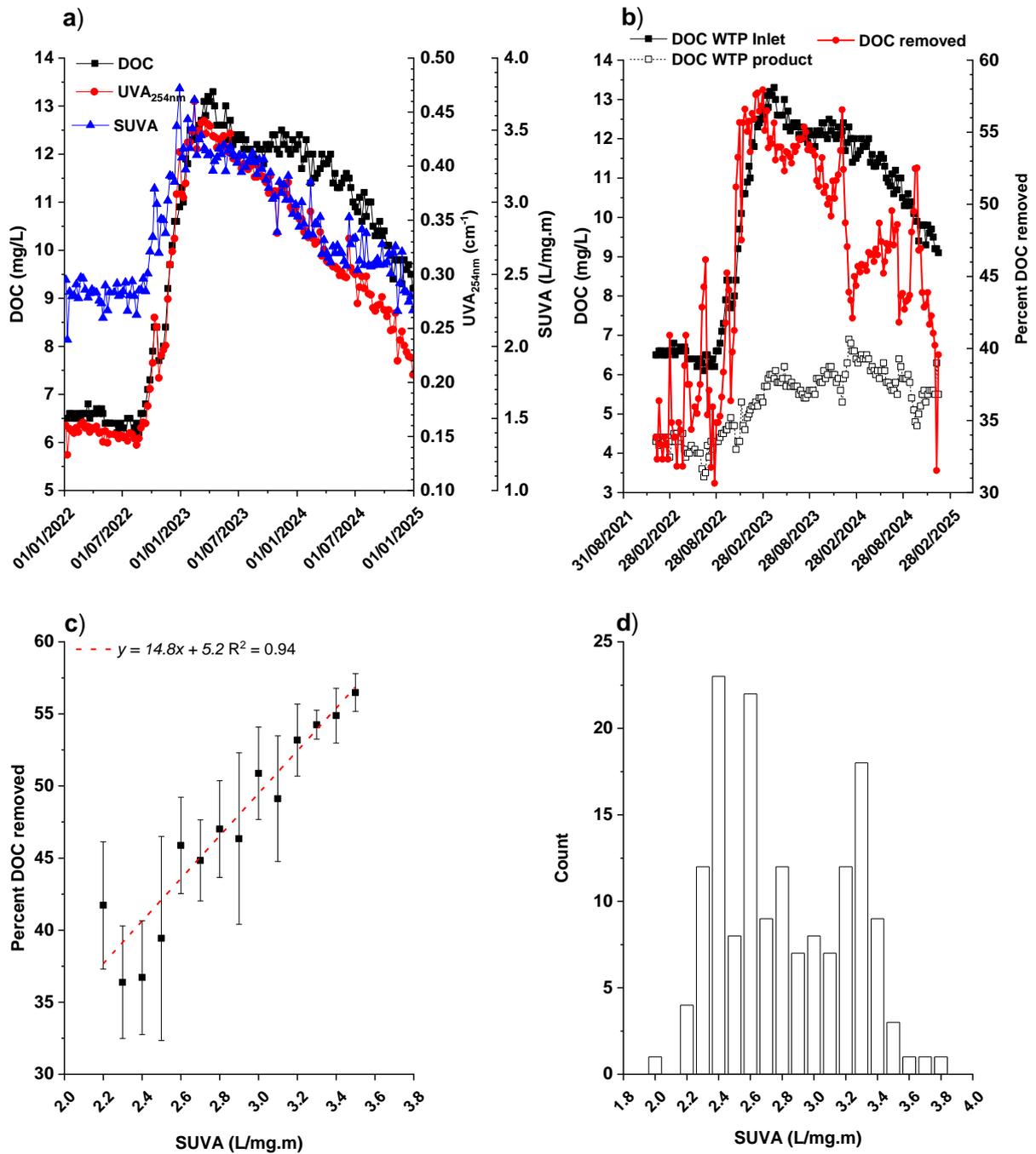


Figure 7. Barossa WTP NOM challenge 2022 – 2025 a) DOC concentration, UVA<sub>254nm</sub> and SUVA, b) DOC inlet, product and percent removal c) percent DOC removal and SUVA and d) histogram of SUVA values

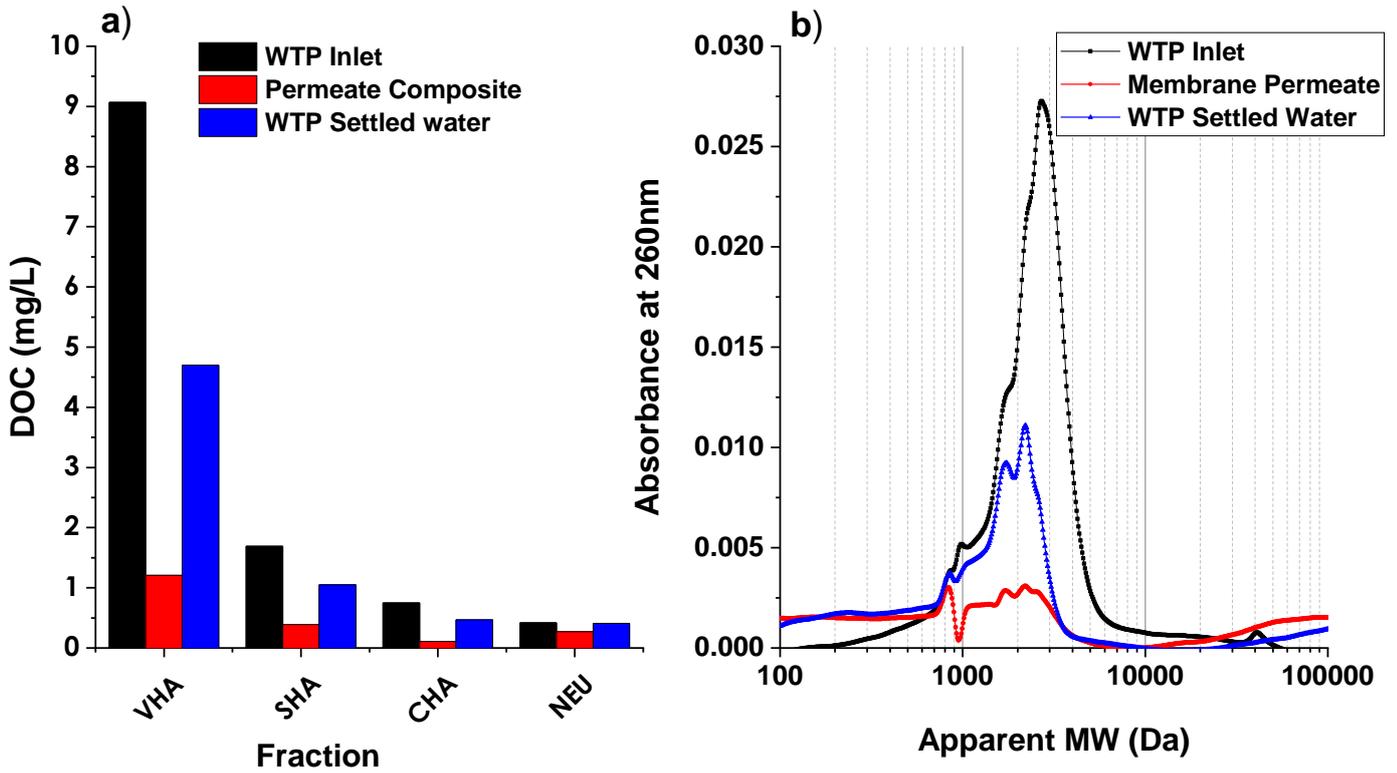


Figure 8. Organic matter characterisation of Barossa WTP inlet, settled and membrane treated water a) Fractionation and b) Molecular weight profile. (VHA = very hydrophobic acids, SHA = slightly hydrophobic acid, CHA = hydrophilic charged, NEU = hydrophilic neutral)

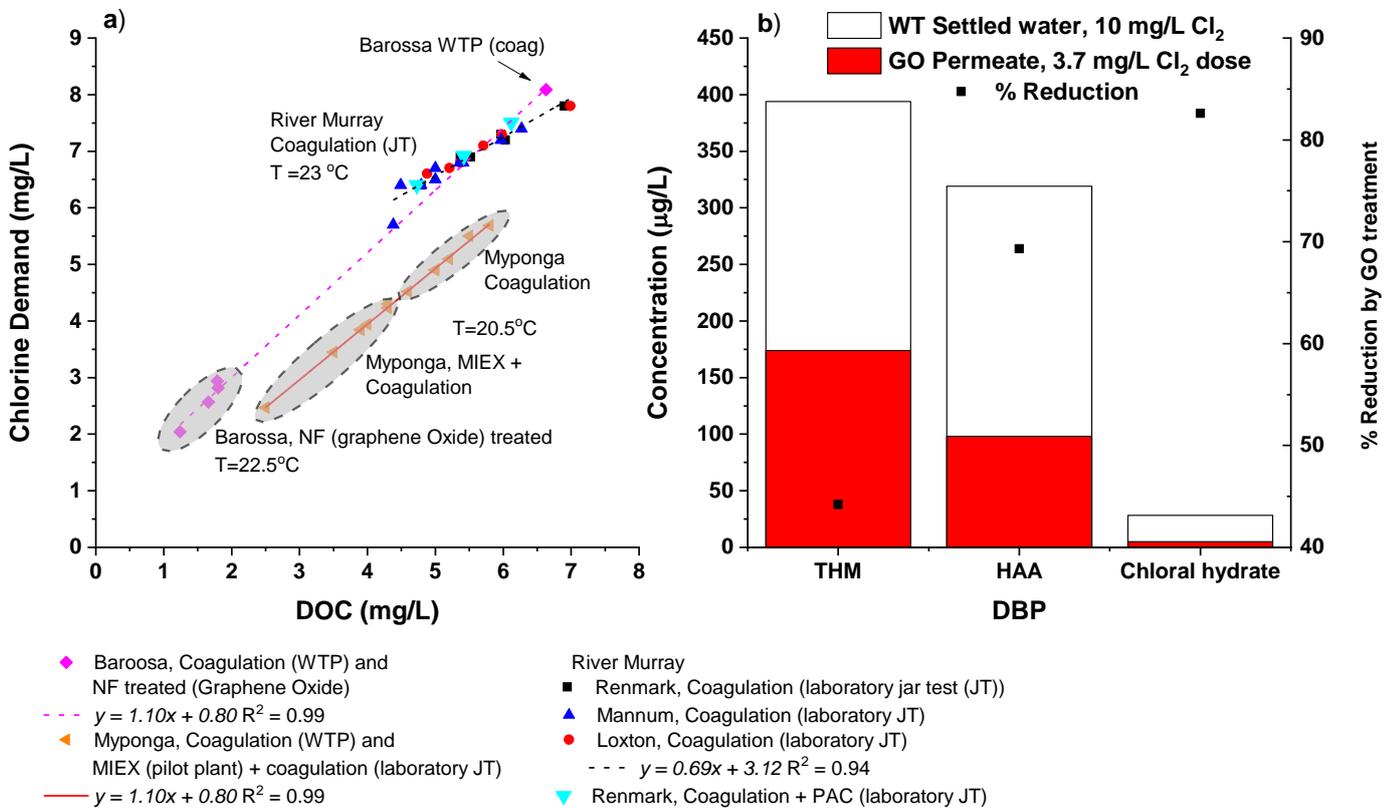


Figure 9. a) Three-day chlorine decay versus treated water DOC of various treated water samples and b) impact of GO membrane treatment on DBP formation after 3 days at 22.5°C