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RESEARCH & INDUSTRY PARTNERSHIPS IN POLAR REGIONS SCIENCE

IMPLICATIONS FOR MUNICIPAL AND ENVIRONMENTAL WATER TREATMENT

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ABSTRACT

Industry participation in water and waste management projects in polar areas presents opportunities for improvement of treatment technologies in the broader global context. For this reason it is useful for industry to build strong partnerships with organisations involved in polar research.

Veolia is working with the University of Melbourne under a five-year Memorandum of Understanding (MoU) to collaborate on research into better water and waste treatment technologies. The first major project is currently focused on sites at Australia's Casey Station, operated by the Australian Antarctic Division (AAD), in East Antarctica. This project aims to utilise low-energy biological processes, such as biofiltration, to remediate summer melt water contaminated with diesel-based hydrocarbons.

The collaboration between Veolia and the University of Melbourne leverages 15 years of Antarctic permeable reactive barrier (PRB) research into ion exchange/adsorption of inorganics and organics, as well as characterisation of biofilms on activated carbon. This has enabled the team to develop advanced analytical techniques for Antarctic research and apply them to more conventional water treatment. Knowledge gained from analysis of carbon samples from Antarctic PRBs has been used to better understand the performance of large-scale biological activated carbon (BAC) filtration processes used in municipal water treatment.

Keywords: Polar regions, biofiltration, activated carbon, R&D partnerships.

INTRODUCTION

Benefits Of Collaborative R&D For Municipal And Environmental Projects

Affordable access to clean water, as well as the appropriate management and treatment of contaminated water, is a major global problem. Human occupation in the polar regions faces the same water management problems, while many of the contributing factors are greatly magnified. For example:

- Water treatment requires energy, and energy costs in cold regions are up to 10 times greater than those in temperate locations;
- Remoteness means that operators need to be self-reliant for skills, and treatment technologies must be robust, simple, and easy to operate and maintain;
- Typically, polar regions have greater ecological sensitivity, hence there is a higher quality requirement for environmental discharge.

The combination of these factors provides a driver for innovation equal to or greater than that of the wider water industry, and developments in technology for polar applications have fast take-up and payback. The exciting extension of this is the opportunity to then take leading edge innovations and apply the same cost reductions and improvements throughout the mainstream water industry.

COLLABORATIVE R&D IN ANTARCTICA – A SHORT HISTORY

Veolia And The AAD

In October 2001, Veolia Environnement and the AAD signed a cooperation agreement in the area of water and waste management in Antarctica. The cooperative agreement was for a period of 10 years (Northcott *et al*., 2014). The 2001 agreement between Veolia and the AAD facilitated a partnership to undertake the first multi-million dollar clean-up campaign in Antarctica. Requiring many years of planning and millions of dollars of investment, the Thala Valley contaminated site remediation commenced in 2003.

Between 1965 and 1986, waste from the occupation of Casey Station was dumped or burned at Thala Valley. This resulted in high concentrations of contamination entering melt streams that formed each summer and drained into the nearby marine environment. To prevent further environmental impacts, the AAD returned waste from the abandoned Thala Valley landfill site, near Casey station in Antarctica. Veolia provided direct investment in the form of

240 waste-specific containers and supported the development of water treatment technologies. This enabled the AAD to repatriate the waste to Australia for further processing and appropriate disposal, and to manage runoff during operations.

The University Of Melbourne And The AAD

The University of Melbourne was a major academic partner in the Thala Valley contaminated site clean-up project. Its contribution was the development of cold-region specific water treatment technologies suitable for contaminated site remediation (Figures 1 to 3). The main areas of focus have been:

- Passive PRB technology for treatment of contaminated groundwater and snow melt; and
- Robust water treatment technologies for treatment of landfill and biopile leachate.

For the Thala Valley site clean-up, a mobile water treatment plant was constructed in a shipping container. The plant was designed to be portable and to run off a generator set so that it could be operated in the field.

The partnership enabled the AAD to demonstrate leadership in waste management matters for the 50 countries that are signatories to the Antarctic Treaty. The partnership also enabled all participating organisations to pool their knowledge and capabilities to develop tools and technologies to address the legacy of station waste left in Antarctica.

Subsequent research between the three partners, with additional input from Victoria University, has included development of an advanced water treatment plant for treating secondary effluent from station wastewater. Developed over a three-year period, this "robust recycling project" resulted in a treatment process that has the capability to treat effluent to potable water quality (Gray *et al*., 2015).

APPLIED BIOFILTRATION RESEARCH

Following on from the work at Thala Valley, Veolia and The University of Melbourne have entered into

Figure 1. PRB installation to capture and treat hydrocarbon contamination from a diesel spill at Casey Station.

Figures 2 and 3. The mobile WTP for the Thala Valley project, designed by the University of Melbourne and built by the AAD.

Figure 4. BAC filters at Kyneton WTP.

a five-year MoU to continue the water and waste management research. Management of diesel-contaminated meltwater and soils remains a key aspect of the collaboration. To this end, investigations include:

- Capture and treatment of contaminants through adsorption and ion exchange processes (Mumford *et al*., 2013);
- Oxidation-reduction processes (Statham *et al*., 2016);
- Characterisation of biofilms on filtration media;
- Influence of nutrients on performance of biofiltration processes (Freidman *et al*., in subm a).

This has enabled Veolia and The University of Melbourne to utilise advanced analytical techniques for Antarctic research and apply them to more conventional water treatment, such as a BAC filter plant at Kyneton (Figure 4). These techniques have facilitated the characterisation of carbon samples from Antarctic PRBs, with the translation of knowledge gained to large-scale BAC filtration processes used in municipal water treatment.

Key research questions that the project partners are interested in include:

- What are the key bacterial species present on BAC that are associated with removal of natural organic matter (NOM), nuisance and toxic organics such as diesel-based hydrocarbons in water?
- What is the fate, and accumulation on activated carbon, of inorganic constituents in water?
- What are the limiting factors for growth of relevant bacterial species on BAC?

The answers to these questions have a significant impact on the management and optimisation of biofiltration processes, in both polar and temperate regions.

METHODS

Monitoring Of Aqua 2000 WTPs

Veolia operates the Kyneton water treatment plant (WTP) under the Aqua 2000 contract with Coliban Water. Kyneton is one of three Aqua 2000 plants commissioned in 2001. All three plants feature ultrafiltration as the primary barrier to pathogens followed by ozone-BAC for disinfection and treatment of dissolved organics and taste and odour compounds. Since 2012 Veolia has implemented an ongoing BAC filter-monitoring program, the aim of which is to track carbon filter media ageing and condition, for better performance management and treatment outcomes.

Activated carbon condition assessment is conducted annually at all Aqua 2000 sites, including the Kyneton BACs. BAC media is sampled at three depths within the 2.5m profile of the filter bed. The samples are tested for the following physical/chemical and biological parameters:

- Physical – iodine number, particle size distribution, volatile content, acid-soluble ash composition, apparent density;
- Microbiological analysis – plate counts.

Treatment performance of the ozone-BAC system is monitored through water sampling and analysis for the following parameters:

- Organic carbon – dissolved organic carbon (DOC), biodegradable dissolved organic carbon (BDOC), assimilable organic carbon (AOC);
- Organics – UV254, colour;
- Nutrients – ammonia, nitrate, total nitrogen, NOx, total phosphorus;
- Metals – soluble iron and manganese.

All of the above are standard analytical techniques used for monitoring and management of activated carbon filters, the results of which have been reported elsewhere (Northcott *et al*., 2015; Thiel *et al.*, 2015). The focus of the collaboration with The University of Melbourne was to apply new and innovative techniques to better understand the role that biofilms play in the long-term performance of BAC filters. These are described further and the results presented in the following sections.

Monitoring Of Antarctic PRBs

To facilitate the translation of knowledge between polar environmental water management and drinking water treatment applications, media used in biofiltration processes were collected from Antarctic field and laboratory studies and compared to municipal water treatment sites. The locations where samples were collected included:

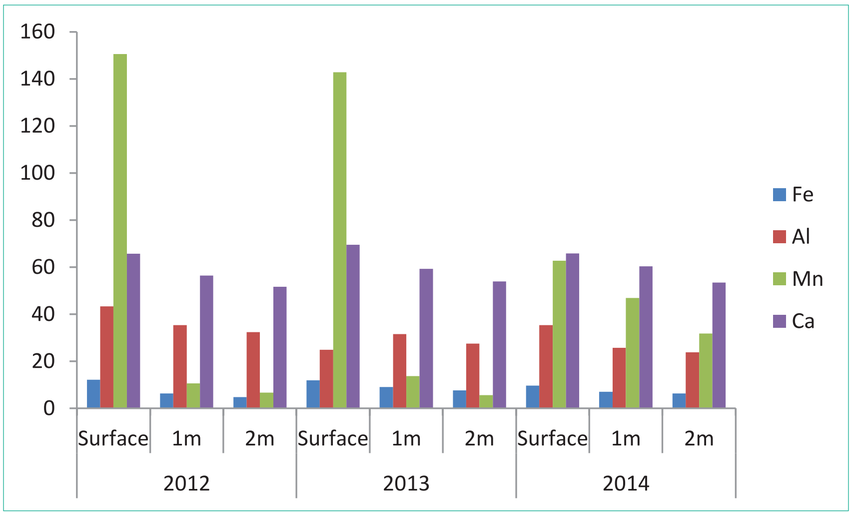


Figure 5. Kyneton BAC filter mineral content trends (mg/g GAC) at three depths, 2012–2014.

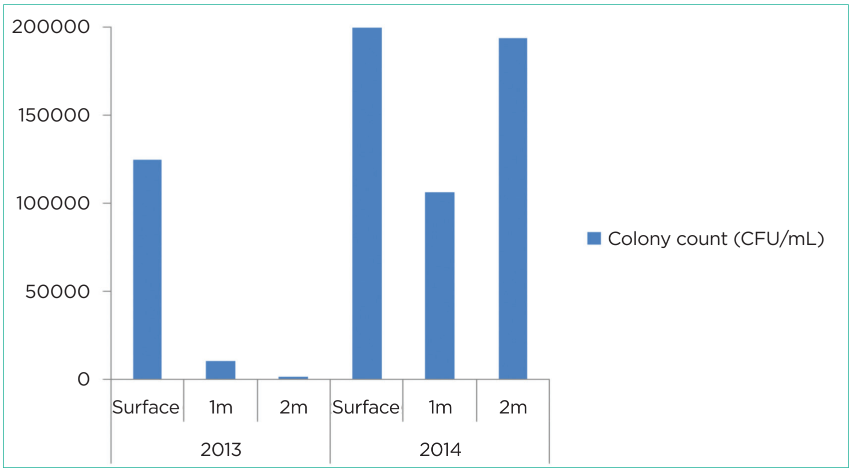


Figure 6. Kyneton BAC filter microbial analysis (CFU/mL) at three depths, 2013–2014.

- PRB at Casey Station, Antarctica, during the 2013–14 summer (Mumford *et al*., 2013). Samples of activated carbon, installed for the adsorption of diesel-based hydrocarbons in Antarctic PRBs, were collected.
- Laboratory-scale PRBs at the University of Melbourne. Samples of a controlled-release nutrient material, ammonium exchanged zeolite, contacted with soil from Old Casey Station, were examined (Freidman *et al*., in subm a).

The Kyneton WTP BAC filter media was chosen for comparative analysis with Antarctic samples, due to the relatively low feedwater operating temperatures for four to five months of the year, commonly between eight and 11°C in the winter months.

Analytical Techniques For Biofilm Characterisation

All BAC and zeolite media were analysed using Field Emission Scanning Electron Microscopy (FESEM). Media surface chemistry was investigated using Energy Dispersive Spectroscopy (EDS) Microanalysis.

Bacterial species identification on the BAC and zeolite was carried out using MALDI-TOF mass spectrometry. The bacteria were cultured on Agar plates and then dried and analysed using the MALDI-TOF mass spectrometer.

X-ray diffraction (XRD) and Raman Spectroscopy were both used to further characterise iron and manganese structures formed through natural bio-mineralisation processes (biogenic minerals). These structures were identified in the electron microscope images (Weiner and Dove, 2003) and then analysed using XRD.

Acid digestions were conducted on media to determine the concentrations of bioavailable iron and manganese (Snape *et al*., 2004). Analysis was conducted using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES).

RESULTS/OUTCOMES

Monitoring Of Municipal BAC filters

Based on current knowledge and industry practice it is considered a combined inorganic contamination loading of 200 mg/g carbon, along with an iodine number at or close to zero, indicates the media no longer has a detectable adsorptive capacity. Trending of carbon media condition (2012–2014) has resulted in effective management of the metals loadings on the media, through backwash optimisation and selective partial carbon change-outs (see Figure 5). This is as a result of a maintenance and asset management program that responds to results from condition monitoring to reduce the impact and prevalence of contamination problems (Thiel, 2014).

Annual microbiological analysis (plate counts) of Kyneton BAC media in 2013 indicated typical levels of micro-organisms in the tens of thousands CFU/mL at the surface, with lower counts at depth. In 2014, however, the colony counts were elevated at one- and two-metre depths, with substantially higher numbers on the surface (see Figure 6).

The recent media and water quality assessments have indicated that, in spite of increasing metals accumulation over time, there has been no evidence of risk of breakthrough of inorganics and no indication of reduction of treatment capacity for organics (Northcott *et al*., 2015; Thiel *et al*., 2015). The increased metals accumulation on the BAC media at Kyneton has also been associated with an increase in microbial colony counts. It was recognised that conventional analytical techniques were insufficient to

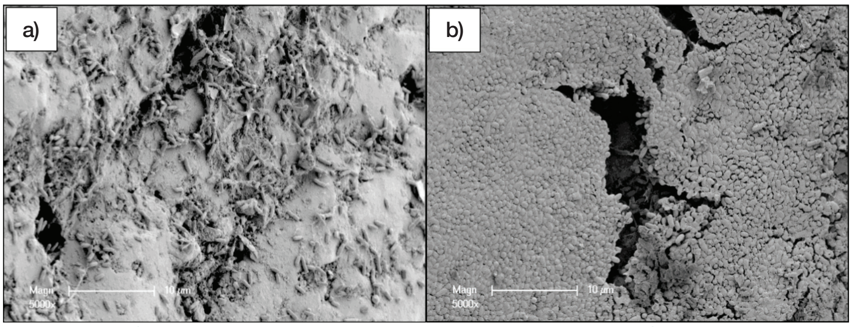


Figure 7. FESEM micrograph of microbial colonisation of BAC media within a PRB at Old Casey Station, East Antarctica (a) and on ammonium-exchanged zeolite in laboratory scale PRBs (b).

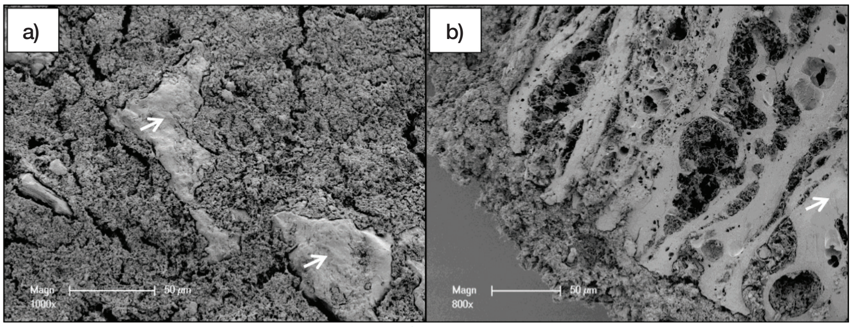


Figure 8. Microbial colonisation of BAC filter surface media at Kyneton WTP (a) and biofilm thickness on carbon sample collected from Kyneton WTP BAC filter (b).

adequately explain what was occurring in the BAC filters, hence the need to explore alternative methods of media analysis.

The following sections describe the work undertaken at The University of Melbourne using advanced analytical techniques to better understand the nature of the biofilms on the BAC filters and the conditions that determine the type, number and diversity of bacterial populations associated with treatment of organics and accumulation of inorganics. This information has been very useful for the ongoing optimisation and management of municipal BAC filters. The results are compared with Antarctic samples to demonstrate the importance of the Antarctic research in development and proving of these techniques.

Microbial Characterisation

FESEM imaging of samples collected from a PRB at Old Casey Station showed mainly rod-shaped bacteria, associated with species with hydrocarbon degrading capabilities (Figure 7a). *Pedomicrobium sp*. were identified, a key species of bacteria associated with biological uptake of iron and manganese in water. However, these bacteria were only present in low numbers in the Antarctic samples, probably due to low concentrations of manganese in the feedwater. Rod-shaped bacteria were often observed in smooth, broad mats across the surface of the ammonium-exchanged zeolite media (Figure 7b).

In contrast to the Antarctic samples, Kyneton BAC filter surface samples were well covered with biomass (Figures 8a and b) (Freidman *et al*. in subm b.). Among the microbial community present, high concentrations of iron and manganese oxidising bacteria were detected in the presence of bioavailable manganese. These included a greater variety of species compared to the Antarctic samples such as *Leptothrix, Pedomicrobium* and *Gallionella,* with a species of *Pedomicrobium* also being identified in Antarctic samples.

Along with the iron and manganese oxidising bacteria, various species of rod-shaped bacteria, such as *Variovirax sp*., were detected, a commonality with samples from Antarctica (see Table 1, asterisk indicates species also identified in Antarctic samples). These bacteria are strongly associated with natural biodegradation processes for organic carbon present in feedwater.

Iron And Manganese Mineralisation – Fate And Accumulation Of Inorganics

Porous spherical minerals were observed on all activated carbon and zeolite water treatment media across Antarctic and municipal filtration applications (see Figures 9a to 9d). The mechanism of formation of these structures is understood to be a result of the presence of the iron and manganese oxidising bacteria. These bacteria induce localised metals precipitation reactions. The precipitates gradually grow into porous rosette-sheeted spheres, comprising organic and inorganic constituents. These structures have a high density and tight binding to the

Table 1. Species identified on BAC media by FESEM imaging and MALDI-TOF analysis (Freidman et al., in subm b.)

Water Treatment Plant	Depth sampled	Genus	Species
Kyneton	Surface	*Pseudomonas* *Aeromonas* *Aeromonas* *Escherichia*	*putida* *bestiarum* *eucrenophilia* *vulneris*
	1m	*Variovorax** *Leptothrix* *Pedomicrobium*	*paradoxus* *discophora* *manganicum*
	2m	*Variovorax** *Leptothrix* *Pedomicrobium* *Pseudomonas*	*paradoxus* *discophora* *manganicum* *putida*

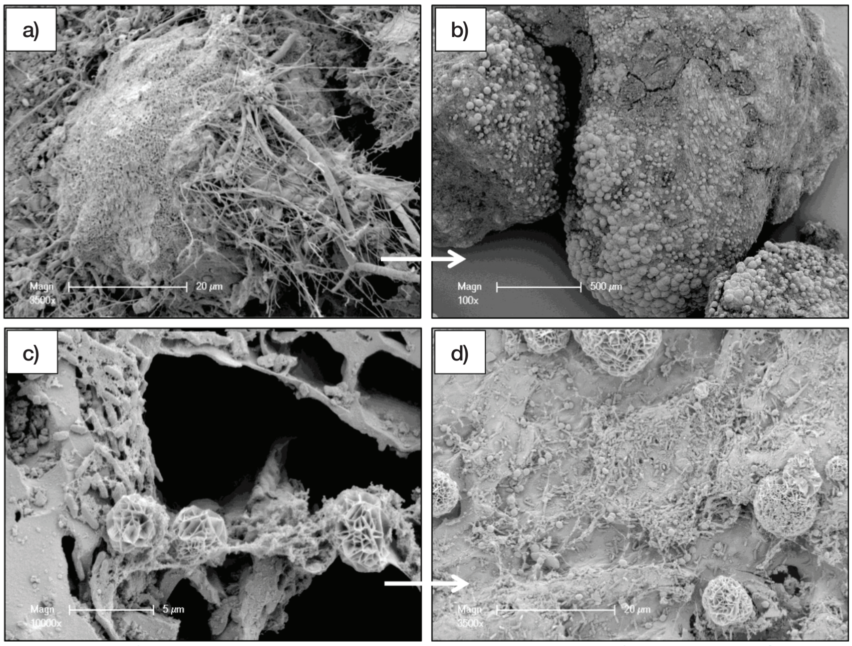
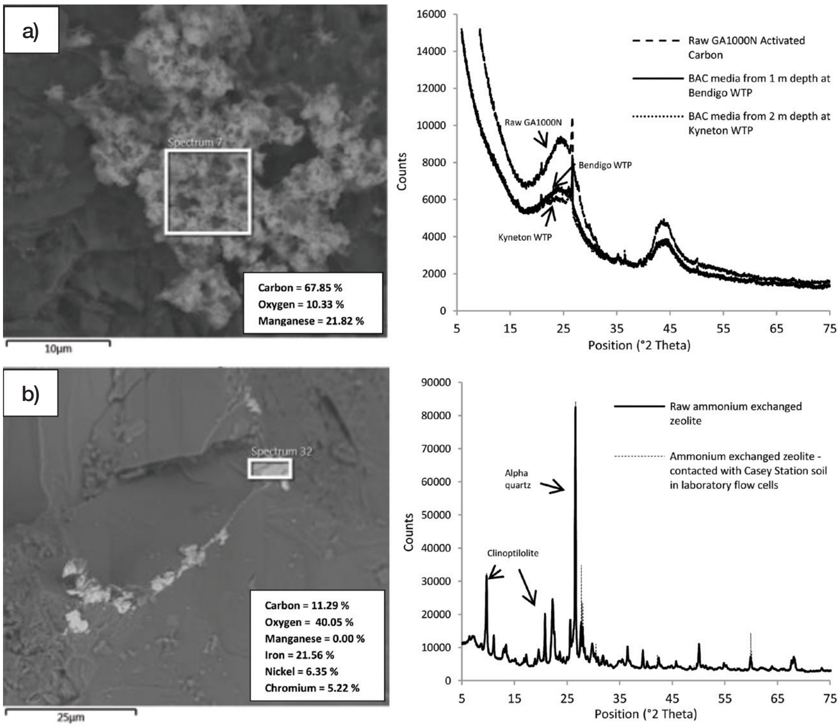


Figure 9. FESEM micrographs of biogenic minerals on BAC filter media (a and b) and on activated carbon and zeolite media from Antarctic field and laboratory PRB studies (c and d).



Figures 10a and b. Energy Dispersive X-Ray Microanalysis of mineral formation on BAC filtration media, and the accompanying XRD spectra (a). Energy Dispersive X-Ray Microanalysis of ammonium exchanged zeolite and accompanying XRD spectra (b). Element percentages represent atomic per cent.

media surface. For all samples tested the morphology of these mineral structures was comparable, indicating a consistent pathway for formation.

The elemental composition of the mineral deposits is presented in Figures 10a and 10b. Iron was shown to be the key building block in deposits on Antarctic BAC and ammonium-exchanged zeolite media, with no detectable manganese. The XRD profile of samples of ammonium-exchanged zeolite contacted with Old Casey Station soil could be attributed to the presence of the iron-based minerals hematite and magnetite (Shopska *et al*., 2012).

In contrast to the Antarctic samples, BAC media samples from the Aqua 2000 plants showed high levels of bioavailable manganese (Figure 10a). XRD analysis of BAC media from the Kyneton WTP identified the formation of manganese oxide minerals birnessite, vernadite and bixbyite (Jiang *et al*., 2010). This was in agreement with the results of Raman spectroscopy analysis.

Elemental analysis of biogenic material structures on Antarctic PRB media clearly showed the uptake of nickel and chromium, with lead and titanium observed in other locations on the media (Figure 10b). This data indicates that biogenic materials offer the potential for the removal of a wide range of aqueous pollutants, including heavy metals.

DISCUSSION

In the context of municipal BAC filtration, the identification of the formation of these biogenic materials signifies an important step in furthering the understanding of long-term development of biofilms. In the past it has been assumed that a loss of adsorption capacity of activated carbon, measured via metals analysis and iodine testing, was indicative of the end of the useful life of the filtration media. This generally triggered a response from the operator of complete change-out of the filtration media, generally a costly and labour-intensive exercise.

Recent studies of BAC filters where adsorption capacity was found to be at or near zero have shown that these filters are still treating water effectively. In particular there have been examples of BAC filters with exceptionally high levels of manganese detected in the media and severely reduced adsorption capacity, which have shown no indication of metals breakthrough and continuing removal of organic carbon (Thiel, 2014).

The biofilm characterisation work described here has potentially important implications for ongoing

Figure 11. Filling the Casey WTP filters with carbon during the 2015–2016 summer season at Casey Station.

treatment capacity and performance of BAC filters, beyond what would normally be considered the useable life of BAC media.

FURTHER WORK

An ongoing need for water treatment to address contamination at Casey Station demonstrates the importance of this collaborative research to the future of environmental protection in the Antarctic. As a result of recent concerns surrounding water quality at Casey Station due to fuel spills, the mobile WTP, originally used for the Thala Valley contaminated site project, has been retrofitted and recommissioned in 2015 and 2016.

The plant has been refitted with granular activated carbon (GAC) filtration to treat hydrocarbon-contaminated melt water and biopile leachate (Figure 11). The advances made in understanding biofilm formation on activated carbon will be crucial to BAC performance optimisation for Antarctic PRBs and municipal BAC filters. This research will continue to expand and develop across the coming field seasons to best inform the ongoing operation of the activated carbon filters in the mobile WTP and PRBs.

CONCLUSION

The collaborative work between Veolia and The University of Melbourne is yielding results that indicate direct comparisons between the behaviour of activated carbon and nutrient-amended zeolite in PRBs in Antarctica, and those of municipal BAC filtration plants in Australia. There are similar bacterial communities present, particularly with those bacteria capable of oxidising dissolved iron and/or manganese. In spite of differing feedwater composition and resulting mineral composition, these bacterial communities produce impressive biogenic mineral structures with strikingly similar morphologies.

Despite the geographical and environmental differences between the Antarctic PRB and municipal BAC filter operations there are a number of similarities in the type and diversity of micro-organisms, and biogenic processes were evident in all samples collected. The techniques for characterisation of the biofilms and the biogenic structures were developed for Antarctic PRBs and then successfully applied to municipal BAC filters.

Utilising the techniques developed for Antarctic PRBs, we have been able to better understand the structure and ecology of biofilms that establish in municipal BAC filters. The retention and accumulation of inorganics through biogenic mineral formation in BAC filters, and their abundance across varying feedwater conditions and media types, suggest that these minerals may extend the performance of activated carbon beyond what would be considered its typical adsorptive capacity

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REFERENCES

Freidman BL, Gras SL, Snape I, Stevens GW & Mumford K (In subm a): Performance of Ammonium Exchanged Zeolite for Biodegradation in Petroleum Hydrocarbon Contaminated Groundwater. *Journal of Hazardous Materials*.

Freidman BL, Northcot t KA, Thiel P, Gras SL, Snape I, Stevens GW & Mumford KA (In subm b): From Urban Municipalities to Polar Bioremediation: The Characterisation and Contribution of Biogenic Minerals for Water Treatment. *Journal of Water and Health*.

Gray S, Zhang J, Duke M, Knight A, Packer M, Northcott K, Hillis P, Dharmabalan D & Scales P (2015): Robust Water Recycling Plant for the Antarctic. AWA Ozwater'15, Adelaide 12–14 May, 2015.

Jiang S, Kim D, Kim J & Ko S (2010): Characterization of the Biogenic Manganese Oxides Produced by *Pseudomonas putida* strain MnB1. *Environmental Engineering Research*, 15, pp 183–190. http://dx.doi.org/10.4491/eer.2010.15.4.183

Northcott K, Snape I, Packer M, Gray S, Scales P, Hillis P, Dharmabalan D & Alcock D (2014): Research & Industry Partnerships for Delivery of Innovative Small Scale Water Recycling Solutions, Small Water & Wastewater Systems Conference, Newcastle, 13–14 August 2014.

Northcott K, Thiel P, Freidman B, Mumford K (2015): Impact of Ozone System Outage on BAC Media Characteristics – Implications for Performance. AWA Ozwater'15, Adelaide 12–14 May, 2015.

Mumford KA, Rayner JL, Snape I, Stark SC, Stevens GW & Gore DB (2013): Design, Installation and Preliminary Testing of a Permeable Reactive Barrier for Diesel Fuel Remediation at Casey Station, Antarctica. *Cold Regions Science and Technology*, 96, pp 96–107. http://dx.doi.org/10.1016/j.coldregions.2013.06.002

Shopska M, Zheleva Z, Paneva DG, Lliev M, Kadinov GB & Mitov IG (2012): Biogenic Iron Compounds: XRD, Mossbauer and FTIR study. *Central European Journal of Chemistry*, 11, pp 215–227.

Snape I, Scouller RC, Stark SC, Stark J, Riddle MJ & Gore DB (2004): Characterisation of the Dilute HCl Extraction Method for the Identification of Metal Contamination in Antarctic Marine Sediments. *Chemosphere*, 57, pp 491–504. http://dx.doi.org/10.1016/j.chemosphere.2004.05.042

Statham TM, Stark SC, Snape I, Stevens GW & Mumford KA (2016): A Permeable Reactive Barrier (PRB) Media Sequence for the Remediation of Heavy Metal and Hydrocarbon Contaminated Water: A Field Assessment at Casey Station, Antarctica. *Chemosphere*, 147, pp 368–375. http://dx.doi.org/10.1016/j.chemosphere.2015.12.133

Thiel P (2014): BAC Ageing Profiles – When Does My Carbon Need Replacement? AWA Ozwater'14, Brisbane, 29 April–1 May 2014.

Thiel P, Northcott K, Freidman B, Mumford K (2015): Optimisation of Microbiology on BAC Filters in the Presence of Ozone, for Drinking Water Treatment. IWA Biofilms Conference, Arosa, Switzerland, 23–26 August 2015.

Weiner S & Dove PM (2003): An Overview of Biomineralization Processes and the Problem of the Vital Effect. *Reviews in Mineralogy and Geochemistry*, 54, pp 1–29. http://dx.doi.org/10.2113/0540001