Determination of Organic Compound Classes Using Research and Regulatory Analytical Techniques for the Demonstration Project

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Abstract

This research demonstrated the ability to track trace-level unregulated contaminants through the treatment train at two water treatment facilities that are within the capture zone of a hazardous waste plume. Sample collection initiated in April 2011 and sampling continued through 2014 at the Merchantville/Pennsauken Water Treatment Plant Marion Avenue Facility (MPW) in Camden County and the Fair Lawn Cadmus Avenue Facility in Bergen County. Each facility utilized air-stripping technology to remove regulated VOC contamination prior to implementation of GAC treatment. This research evaluated the removal/reduction efficiency of physical adsorption technologies to reduce the levels of trace organic compounds using three types of commercially available granular activated carbon (GAC). Monitoring the actual efficiency of the removal media, like granular activated carbon, does not routinely occur at low parts-per-trillion concentration levels. Typically, pilot or bench-scale column studies have focused on sorptive capacity with spiked chemicals at part-per-million concentrations rather than ambient level, (part-per-trillion), concentrations to determine removal efficiency. Often the media is evaluated at concentrations that are orders of magnitude higher than the levels in the water due to limitations of traditional measurement methods. Thus, the sorption efficiency, molecular diffusion into the GAC pore structure, and other physical sorption phenomena do not represent the trace organic matrix condition that the media is actually exposed to under normal operational conditions. Therefore, it was the objective of this study to measure the efficiency of the media at ambient parts per trillion levels. This research utilized both optimized regulatory analytical methodology in conjunction with state-of-the-art analytical research methods to determine the full scale activated carbon treatment removal efficiencies of unregulated contaminants in ground water. Although the three different carbon types evaluated were similar in performance, the data indicated that performance differences existed in the GAC material and were related to the polarity of the observed unregulated contaminants. The New Jersey Department of Health analytical method identified very low levels of unregulated nonpolar contaminants throughout the drinking water treatment train. The percentage of TICs removed to below detection limit as analyzed by the 525.2LL method for both systems represented a 91-99% reduction. On the other hand, the Rutgers EOHSI laboratory technique identified a select few, more-polar compounds, which passed through the treatment train to delivered drinking water. The percentage of TICs removed to below detection limit as analyzed by the Solid Phase Micro Extraction (SPME) method for both systems represented a 72-85% reduction. Given the difference in preferential adsorption and removal by the GAC materials, none of the three carbon types can be used alone to remove the full suite of observed polar and non-polar organic compounds.

Introduction

The need for this project arose from the realization that the Division of Science, Research, and Environmental Health (DSREH) needed to use advanced analytical techniques to determine the efficiency of carbon contactors being constructed as part of a demonstration project designed to reduce the concentration of unregulated contaminants that resulted from known contamination within the capture zone of two public ground water supplies in the State. Previous DSREH source water and drinking water research projects identified many unregulated contaminants (synthetic organic chemicals, SOC) at low levels in these locations (Louis et al., 2010). Both facilities met or exceeded the water quality standards of the USEPA and State of New Jersey for regulated contaminants including volatile organic compounds (VOCs), for which a remedial water treatment strategy (air stripping) has been implemented at both facilities. Existing regulatory analytical techniques such as gas chromatography/mass spectrometry (GC/MS) cannot be used in all situations because there are many non-volatile and polar compounds in ground water that may pose as much of a threat as the regulated semi-volatile contaminants. We have previously used identification of semi-volatile organic compounds to identify groundwater supplies that were subject to contamination from adjacent contaminated sites. Semi-volatile organic compounds can be identified by comparing the mass spectra to those obtained from commercially available compounds or to existing libraries of organic compounds that are commercially available. This cannot be done for the nonvolatile or polar compounds because no such database currently exists.

The objectives of this study were to:

(1) Investigate how three different commercially available granular activated carbon media influenced the removal of synthetic organic compounds and natural (macromolecular) materials.

(2) Identify adsorbent characteristics between these three carbon types that optimize the uptake of SOCs and naturally occurring organic materials (NOM)s, potentially demonstrating a full range of compound class coverage.

(3) Provide the purveyors of these facilities with an assessment of the efficiency of GAC as a barrier technology for removal of a broad spectrum of trace organic contaminants and assess the potential life span of the filtration media.

Methods

Two locations were selected for this study; Merchantville/Pennsauken Water Treatment Plant Marion Avenue Facility (MPW) in Camden County and the Fair Lawn Cadmus Avenue Facility in Bergen County. At MPW, a total of three identical pressure vessels are arranged into three parallel flow configurations. The carbon contactors at the Fair Lawn water treatment facility are configured differently with the pressure vessels arranged in a lead-lag flow path with two parallel trains.

Three media types were utilized to evaluate their efficiency at removing chemicals of concern. They included Filtrasorb 300, Filtrasorb 600, and coconut shell. All three media were installed at Merchantville/Pennsauken while only the Filtrasorb 300 and coconut shell materials were installed at Fair Lawn. Filtrasorb 300 and Filtrasorb 600 are produced by Calgon™ and produced from a pulverized blend of high quality bituminous and lignite coals resulting in a consistent, high quality product. Coconut granular activated carbon is designed for odor and VOC removal in vapor applications. It is made from select grades of coconut shell that imparts a hardness that is necessary for the long life expected in many applications.

Each sample drawn for this project generated six separate analyses. We tested two different isolation techniques, Solid Phase Extraction (SPE) (modified USEPA method 525.2 low level analysis [525.2LL] at the NJ Department of Health (NJDOH) Public Health and Environmental Analytical Laboratory (PHEAL) laboratory and Solid Phase Micro Extraction (SPME) research methods at Rutgers University Environmental and Occupational Health Sciences Institute (EOHSI) laboratory. The SPME technique uses two modes of isolation, the headspace mode for purgeable organic compounds and the immersion mode for water soluble analytes.

Isolation and Analysis at NJDOH

The 525.2 low level analysis conducted at NJDOH uses a non-polar (C18) stationary phase on the 525.2LL SPE filter disk that is used to extract the sample. Therefore, non-polar chemicals will preferentially adsorb to the filter disk surface. The modified regulatory method 525.2 Low Level analysis conducted by NJDOH targets a fixed class of known regulated compounds, but reports tentatively identified compounds (TICs) in addition to the standard parameter list.

Research Isolation and Analysis at Rutgers University

The Solid Phase Micro Extraction technique developed at EOHSI used a solid sorbent material on a silica bed surrounded by a stainless steel needle to trap semi-volatile analytes either directly from a water sample or in the headspace above the water sample. The solid material is similar to a GC solid phase establishing an equilibrium between the sorbent material and the sample matrix or headspace. This allows for multiple analysis of the same sample, generally without significant depletion of the analyte. It is ideal for semi-volatile chemical analysis because the sample can be heated to release the analytes from the matrix but is more versatile than a purge and trap system because it works directly with water samples. There is more than one type of sorbent material used and it has been determined here that in addition to leaching time, ionic strength of the water sample, agitation rate and other controlled variables, a compound's affinity for the sorbent affects the methods overall sensitivity. The SPME method is simple, direct, and once optimized, capable of providing data on hundreds, if not thousands, of polar volatile and semi-volatile compounds in water samples. Coupled with a substantial MS library, most of the compounds detected by the GC/MS protocol can be identified.

Mass Spectra Data Filtering

Laboratory analysis sample results were supplied by the NJDOH and EOHSI laboratories in spreadsheet format. These data not only contained the chemical identity of the regulated parameters that were part of the 525.2LL USEPA method, but additional tentatively identified parameters that were detected by the low-level analysis as well. For example, one data file from the EOHSI laboratory file for Fair Lawn contained over 3,267 tentatively identified chemical compounds (TICs) from nineteen samples that were collected from this facility on 3/22/2012. A data reduction strategy was needed to reduce the quantity of detected compounds and determine their relevance to the primary objective of the study.

The first step in the mass spectral data reduction process was the subtraction of TICs that were identified in the field and trip blanks. In addition, all compounds containing siloxane in the name were removed as likely to come from the GC column bleed. This data reduction operation greatly reduced the number of TICs identified in the combined effluents to 264 and 114 for the Fair Lawn and Merchantville/Pennsauken samples, respectively (Tables 1). This reflects a 72.3% and 84.7% reduction in the number of identified TICs after accounting for those identified in blanks. Additionally, only a small

number of TICs were observed at multiple sampling locations throughout the treatment processes at Fairlawn and Merchantville/ Pennsauken (Table 1). The remaining TICs were then custom filtered by concentration to identify and evaluate unique chemicals of concern and then sorted again by occurrence in each contactor, bed depth level, and combined effluent from the GAC unit operation. In similar fashion, a 99.1% and 90.8% reduction in the number of identified TICs after accounting for those identified in blanks was observed using the 525.2 LL determination by the NJDOH PHEAL laboratory. Overall, 21 and 19 compounds were detected at multiple sampling locations throughout the treatment processes using the 525.2 LL method (Table 2).

Table 1. Mass spectral data filtering summary of the Rutgers EOSHI research method results of tentatively identified compounds (TICs) for Fair Lawn and Merchantville/Pennsauken facilities.[1]		
Mass Spectral Data Set	Number of TICs at Fair Lawn	Number of TICs at Merchantville/Pennsauken
Total TICs detected in raw water (after air-stripping)	3,267	1,521
TICs detected after subtracting those identified in field and trip blanks	952	747
TICs detected in the combined effluent	264	114
Removal efficiency	72.3%	84.7%
TICs detected at multiple sampling locations through the treatment System	24	34
[1] The Fairlawn sample was collected 03/22/2012 and the Merchantville/Pennsauken sample was collected 04/19/2011. Counts reflect the number of TICs identified throughout the treatment train.		

Table 2. Mass spectral data filtering summary of the NJDOH method results of tentatively identified compounds (TICs) for Fair Lawn and Merchantville/Pennsauken facilities.[1]		
Mass Spectral Data Set	Number of TICs at Fair Lawn	Number of TICs at Merchantville/Pennsauken
Total TICs detected in raw water (after air-stripping)	3,127	3,052
TICs detected after subtracting those identified in field and trip blanks	706	796
TICs detected in the combined effluent	6	73
Removal efficiency	99.1%	90.8%
TICs detected at multiple sampling locations through the treatment System	21	19
[1] The Fairlawn sample was collected 03/22/2012 and the Merchantville/Pennsauken sample was collected 04/19/2011. Counts reflect the number of TICs identified throughout the treatment train.		

Results

Results evaluating the preferential adsorptive performance of each carbon type at both facilities for all sample campaigns for chemicals that could be tracked consistently through the water treatment process are summarized in Table 3. This summary reflects compounds found in the effluent and at least two or more other locations throughout the carbon filtration units. This evaluation is based on the relative efficiency of each carbon type for removal of different polar and nonpolar contaminants. Figures were prepared and included in the full project report (Lippincott and Buckley, 2017) for each compound that was identified using the mass spectral data. Figure 1 is an example figure based on the Merchantville/Pennsauken facility findings for the chemical 1-Methyl-2-Pyrrolidone. Figure 1 shows that 1-Methyl-2-Pyrrolidone was detected multiple times at various coconut shell and Filtrasorb 600 media depths, but only one detection of this compound was found in the aqueous phase throughout the Filtrasorb 300 media. This suggests that the Filtrasorb 300 has better sorptive capability for 1-Methyl-2-Pyrrolidone. These figures can be used to aid in the determination and selection of the optimum carbon type adsorption performance.
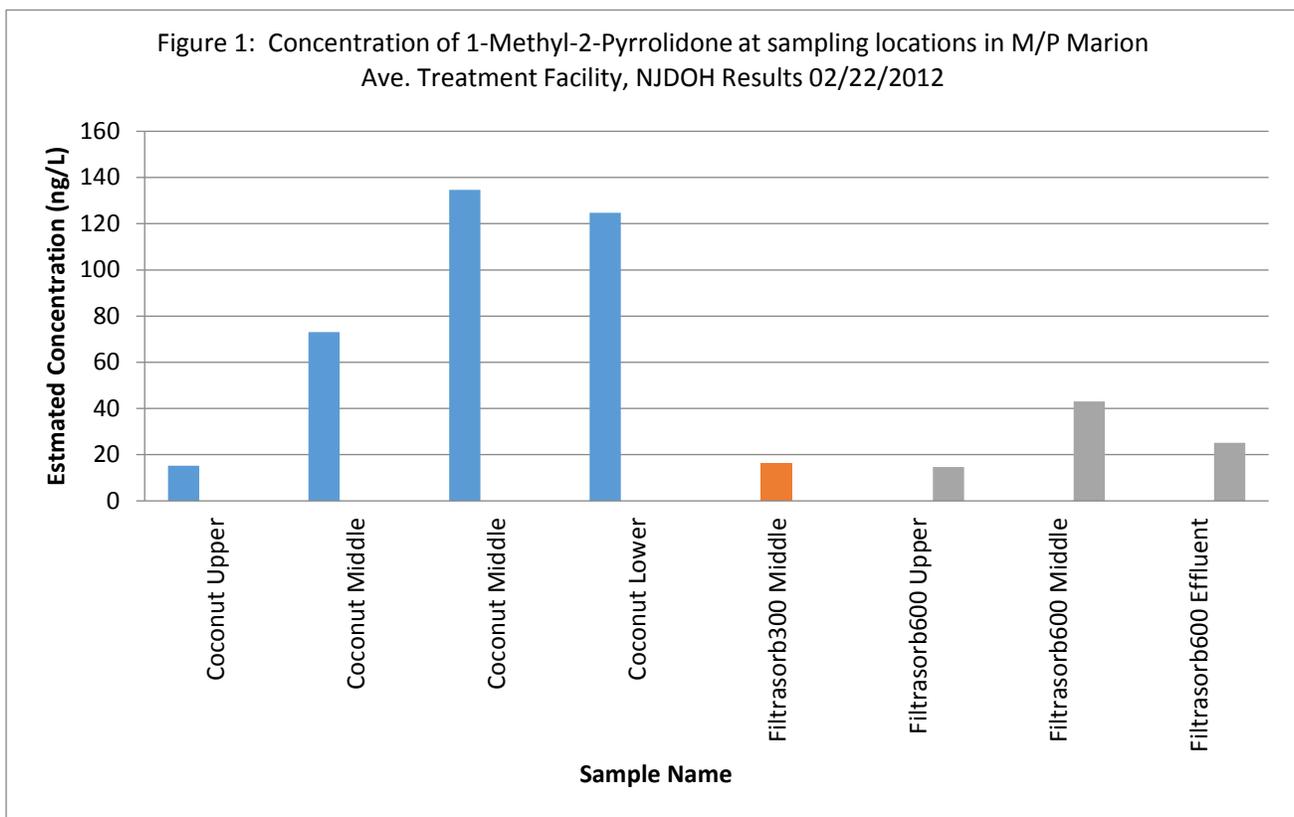

Figure 1: Concentration of 1-Methyl-2-Pyrrolidone at sampling locations in M/P Marion Ave. Treatment Facility, NJDOH Results 02/22/2012

Facility	Coconut Shell	Filtrasorb 300	Filtrasorb 600
MP	9-Hexadecenoic acid [2]	1,1-Diphenyl-2-cyano-2-carbo-octoxy-acetylene [2]	4-methyl-1,3-Benzenediamine[1]
MP	9-Octadecenamide [2]	1,2-Benzenedicarboxylic acid, diisononyl ester [2]	2-(2-ethoxyethoxy)- Ethanol [1]
MP	Hexadecane [2]	Myristic Acid [2]	1-Octadecene [2]
MP	9-Octadecenoic acid [2]	Benzoic acid [2]	Isopropyl Myristate [2]
MP	Propanoic acid, 2-methyl-, 1-(1,1-dimethyl) [1]	Erythro-9,10-dihydroxyoctadecanoic acid [1]	9-octyl-Heptadecane [2]
MP	Stephabyssine [1]	2-Nonadecanone 2,4-dinitrophenylhydrazine [1]	2,6-bis(1,1-dimethylethyl)-4-ethyl- Phenol, [1]
MP		1-Methyl-2-Pyrrolidone	
MP		3-phenyl-2-Propenal, [1]	
MP		15-Hydroxy-7-oxodehydroabietic acid, methyl ester [1]	
MP		Cholestan-3-one, cyclic 1,2-ethanediyl a [1]	
FL	2-(bicyclo[2.2.1] hept-5-en-2-ylidene) propanediol [2]	1,2 Benzenedicarboxylic Acid [2]	
FL	1-bromo-2-chloro-Benzene [2]	Dibutyl Ester of 1,2 Benzenedicarboxylic Acid [2]	
FL		Tetrachloro-1,3-Isobenzofurandione [2]	
FL		Cyclododecane [2]	

Table 3. Summary of assumed preferential adsorption media type for polar organic compounds identified by the Rutgers SPME method[1] and nonpolar compounds identified by the NJDOH 525.2 LL method[2] at the Merchantville/Pennsauken (MP) and Fair Lawn (FL) Cadmus Avenue treatment plants.

Preferential adsorption was assessed by comparing the relative concentrations of each compound in the aqueous phase across each media, i.e. the media type with the lowest aqueous–phase concentration had the greatest adsorption potential. This summary reflects compounds identified from all sample campaigns and were found in the effluent and at least two or more other locations throughout the carbon filtration units. Filtrasorb 600 was not analyzed at Fair Lawn.

Discussion & Conclusions

A new GC/MS scanning method with a data search filter was applied to water samples collected from two purveyors who installed GAC as an additional water treatment method to remove unregulated trace organic chemicals from treated water. Both synthetic organic chemicals and natural organic chemical products derived from plant decay were isolated and identified using the Rutgers EOHSI analytical techniques and the NJDOH optimized regulatory method 525.2 Low Level, with over 60 samples from the Marion Avenue facility in Merchantville/Pennsauken. These samples were collected from various depths in the three carbon contactors with different adsorption media (coconut shell, Filtrasorb 300, and Filtrasorb 600). Of the natural products that were isolated only a few were identified in every sample. For example, many sterol compounds that appeared only sporadically in the samples were eliminated using a data filter of the mass spectral library searches. These sterols are structurally similar to each other through a cholesterol backbone arrangement that imparts biological activity that may affect endocrine systems.

This research demonstrated the ability to track trace-level unregulated contaminants through the treatment train at two facilities that are within the capture zone of a hazardous waste plume. Each facility utilized air-stripping technology to remove regulated the VOC contamination prior to implementation of GAC treatment. Although the three different carbon types evaluated were similar in performance, the data indicated that performance differences existed in the GAC material and were related to the polarity of the observed unregulated contaminants. In terms of preferential adsorption and removal by GAC, the following was observed:

- Coconut shell carbon showed preferential adsorption for low molecular weight polar organic compounds like the three-carbon substituted acid, Propanoic acid, 2-methyl-, 1-(1,1-dimethyl) [Final report, Appendix 2, pg.44].
- Filtrasorb 600 product showed superior sorptive performance for long chain nonpolar compounds, like 9-octyl-Heptadecane [Final report, Appendix 2, pg.61], but was less efficient for polar trace organic contaminants.
- More polar compounds showed increased sorption on the Filtrasorb 300. The compound 1- Methyl-2-Pyrrolidone [Final report, Appendix 2, pg.50], is an example of the efficiency for Filtrasorb 300.

Additionally, the NJDOH analytical method identified very low levels of unregulated nonpolar contaminants throughout the drinking water treatment train. The percentage of TICs removed to below detection limit as analyzed by the 525.2LL method for both systems represented a 91-99% reduction. On the other hand, the EOHSI laboratory technique identified a select few, more-polar compounds, which passed through the treatment train to delivered drinking water. The percentage of TICs removed to below detection limit as analyzed by the Solid Phase Micro Extraction (SPME) method for both systems represented a 72-85% reduction. Given the difference in preferential adsorption and removal of the GAC materials, none of the three carbon types can be used alone to remove the full suite of observed polar and non-polar organic compounds. This research can be used as guidance to tailor an appropriate removal strategy for particular water-quality needs. Further research could be performed to determine if each media type would remain as effective if bed materials were combined in a single vessel or if the three media types were staged in series.

For these two locations GAC treatment served as a sufficient barrier for many unregulated organic contaminants. Media change out was specified in the conditions of the permit and was

to be determined based on breakthrough of regulated pesticide compounds. Breakthrough was reported after four years of continuous operation. These two locations are similar to other locations in the State, but the effective life span of the treatment material will vary from location to location depending on water-quality, water demand, and contact times within the media vessels.

Recommendations for Future Research

Further research could be performed to determine if each GAC media type would remain as effective if bed materials were combined in a single vessel or if the three media types were staged in series. In addition, an extraction of the spent carbon material from each contactor upon changeout of the GAC could show additional parameters that were sorbed to each carbon type over the service life of the media.

Organic chemical analyses have also advanced through the development of lower cost high resolution gas and liquid chromatographs with high resolution mass spectrometer detectors. The NJDOH laboratory has recently purchased an HRGC/MS as part of their suite of advanced analytical instrumentation. In addition, the advanced quantitative time of flight (Q-TOF) mass spectrometer detectors preserve the entire mass spectral record of all analyzable compounds in a sample. Coupled with the current data acquisition, and data reduction tools, identification of unknown organic compounds in the environment is greatly simplified with sensitivities in the ng/L range. These new analytical tools offer the ability to enhance our knowledge of the efficiency of the drinking and wastewater treatment processes so that they may be further optimized for enhanced treatment capability.

References

Lippincott, L. and B. Buckley. 2017. Determination of Organic Compound Classes Using Research and Regulatory Analytical Techniques for the Demonstration Project. Public Water Systems (PWS) Groundwater Investigation at Merchantville/Pennsauken and Fair Lawn Water Treatment Facilities. SR08-049. New Jersey Department of Environmental Protection, Division of Science, Research, and Environmental Health.

Louis, J., G. Carter, L. Lippincott, M. Yoon, B. Buckley, and E. Murphy. 2010 Measuring Groundwater Contamination within Source Water Protection Zones Using HPLC/MS: Techniques to Complement Existing Analytical Methods. Research Project Summary. New Jersey Department of Environmental Protection, Office of Science and Research.

Acknowledgements

which would improve the water quality for their individual communities.

RESEARCH PROJECT SUMMARY

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