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Pyrogenic Activity of Carbon-Filtered Waters

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16. ABSTRACT The endotoxin content and pyrogenic response of granular activated carbon (GAC) filtered waters were studied. GAC-filtered secondary effluent from an activated sludge pilot plant contained free endotoxins in the range 6-250 µg/l yielding positive pyrogenic responses in 18 of 20 trials. Samples obtained from 27 different water supplies in the U.S. that utilize GAC adsorption contained free endotoxin ranging from 1.2-25 µg/l but none gave a pyrogenic response. No relationship was discernible between endotoxin content and pyrogenic response.

Small removals of total organic carbon (TOC) by GAC beds which had been in operation in water treatment plants without regeneration for as long as 110 months were observed. However, 5 of 28 samples showed an increase in TOC through GAC and 8 of 28 samples showed an increase in standard plate count. One of 25 samples yielded pseudomonads, but none of the 28 samples contained coliforms.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our national environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The primary mission of the Health Effects Research Laboratory in Cincinnati (HERL) is to provide a sound health effects data base in support of the regulatory activities of the EPA. To this end, HERL conducts a research program to identify, characterize, and quantitate harmful effects of pollutants that may result from exposure to chemical, physical, or biological agents found in the environment. In addition to the valuable health information generated by these activities, new research techniques and methods are being developed that contribute to a better understanding of human biochemical and physiological functions, and how these functions are altered by low-level insults.

This report describes the endotoxin content and pyrogenic response found in granular activated carbon filtered waters. With a better understanding of any health effects, measures can be developed to reduce exposure to potentially harmful materials.

R. J. Garner
Director
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ABSTRACT

The endotoxin content and pyrogenic response of granular activated carbon (GAC) filtered waters were studied. GAC-filtered secondary effluent from an activated sludge pilot plant contained free endotoxins in the range 6-250 μg/l yielding positive pyrogenic responses in 18 of 20 trials. Samples obtained from 27 different water supplies in the U.S. that utilize GAC adsorption contained free endotoxin ranging from 1.2-25 μg/l but none gave a pyrogenic response. No relationship was discernible between endotoxin content and pyrogenic response.

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This report was submitted in fulfillment of Grant No. R-804420 by Texas A&M University, under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period March 9, 1976 to July 31, 1978, and work was completed as of August 29, 1978.

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PYROGENIC ACTIVITY OF CARBON-FILTERED WATERS

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INTRODUCTION

The efforts of U.S. Environmental Protection Agency (EPA) programs relating to water pollution control and drinking water safety are resulting in increased emphases on conservation of the water resource and its reuse--but with an over-riding and dominant concern for protection of the public health. Among the agents in water of health concern are some of the organic chemicals -- particularly those commonly grouped as trihalomethanes (THMS) and as synthetics (chemical products produced by man). The unit process employed in water and waste water treatment that appears most promising in providing for a greater degree of control of these unwanted organic chemical substances is activated carbon adsorption.

Activated carbon has a long history of use in both water and waste water treatment. It is available in powdered and granular forms. The powdered form has found its greatest use in water treatment. Granular activated carbon (GAC) has been the form most used in waste water treatment, but this use has been largely restricted to pilot studies. Full-scale plant use of GAC is rare in waste water treatment, Garland, Texas, being a notable example.

Although the GAC function is primarily adsorptive, the observation of a concomitant biological activity has long been observed. In fact, the observation of some denitrification occurring in GAC adsorption columns at the Pomona, California, advanced waste treatment (AWT) pilot plant gave rise to successful experiments designed to enhance this biological process by providing a cheap carbon source via the addition of stoichiometric amounts of methanol. The use of biological processes to treat waste water is common, but the use of such processes to treat drinking water (i.e., water for drinking purposes) raises many apprehensions. A whole generation of engineers schooled in the physical-chemical treatment of water has been produced; few have aquaintance with the former use of slow sand filters in water treatment which process is to a great extent biological.

In addition to this general apprehension, there is the caution expressed by Dr. Joshua Lederberg, Nobel laureate geneticist from Stanford University, who reminded the National Drinking Water Advisory Council of the EPA that man still does not have a complete understanding of the carbon cycle. Nevertheless, he also encouraged the thorough research and application of adsorptive processes as the most promising tools available to obtain better control of unwanted organic substances in our drinking water supplies.

The observation of substantial biological activity in GAC treatment of waste water does not prove that a similar degree of such activity will occur when treating drinking water. Source waters used for potable supplies have considerably smaller amounts of biodegradable materials than do biologically treated waste waters. Also, water treatment processes frequently employ preliminary disinfection (prechlorination) as well as coagulation, flocculation, and sedimentation techniques with the result that the waters that would reach a GAC process would be of considerably higher quality than in a waste water application. Nonetheless, some degree of biological development in a water treatment application of GAC would be certain.

One of the main concerns about biological growth in GAC filters or beds is the potential for generation of unwanted microorganisms and/or their toxic by-products. Among the microorganisms that might become established are the pseudomonads. They are known for their ubiquity, growth in minimal media, and their importance in denitrification (1). Also, some strains are opportunistic pathogens of man.

Among the toxic by-products to be aware of are the gram-negative endotoxins. Gram-negative endotoxins are lipopolysaccharides which are all thought to cause a pyrogenic response (fever) when injected into animals. The rabbit is used in the standard United States Pharmacopeia (USP) pyrogen test (2), but man can reportedly be 100-fold more sensitive to endotoxins than is the rabbit (3).

Although some lipopolysaccharides will elicit a toxic response in some individual animals when ingested in sufficient amounts, it is supposed to occur only as a result of an increased permeability of the gastrointestinal tract. Contention apparently exists about this point since it is reported that the observation of absorption of endotoxin by the normal bowel is disputed (4). Certainly, the normal bowel of most mammals contains a generous supply of endotoxins (5).

Just as different animals possess different sensitivities to endotoxin, so do different bacteria produce toxins of different toxicity. The recently developed Limulus Amebocyte Lysate (LAL) assay for gram-negative endotoxins includes within its measure lipopolysaccharides from organisms which are not particularly endotoxic. Originally described by Levin and Bang (6), the assay can detect as little as 1 nanogram of bacterial endotoxin per milliliter (or 1 μg/l) in a period of less than two hours. The test is reportedly simple, specific, and rapid, and inexpensive when compared to the USP rabbit pyrogen test (2). It has found use in detecting clinical endotoxemia as well as for the detection of bacterial endotoxins (pyrogens) in biological products and other drugs or fluids for parenteral administration to man (7,8).

The LAL assay was first described in an environmental application by DiLuzio and Friedmann (9). They had observed gram-negative endotoxin contamination of their dionized water, then found endotoxins in New Orleans tap water, and -- curiosity getting the better of them -- went on to examine a host of different waters. Their results are reproduced in Table 1. Additionally, they reported Mexico City tap water at 800 μg/ml, a commercially bottled water from Mexico City as negative, random samples of beer,

TABLE 1. ENDOTOXIN CONTENT OF CERTAIN MUNICIPAL DRINKING WATERS, MISSISSIPPI RIVER WATER, THE GULF OF MEXICO, AND ADJACENT BAYS (9)

Sample tested	Water source	Endo-toxin	Endotoxin concentration ($\mu g\ ml^{-1}$)
Drinking water			
Baltimore, Md.	Reservoirs	+	
Chicago, Ill.	Lake Michigan	+	
Denver, Colo.	South Platt River and streams from Bear Creek	+	10
Galveston, Texas	Artesian wells	+	
Harrisburg, Pa.	Reservoir	+	
Hazelton, Pa.	Reservoir	+	
Kalamazoo, Mich.	Artesian well	—	
Knoxville, Tenn.	Fort Loudoun Lake	+	
Las Vegas, Nev.	Lake Mead (60%)	+	
	Wells (40%)	+	
Little Rock, Ark.	Lake Maumelle	+	
	Lake Winnoa		
Los Angeles, Cal.	Wells (12%) Colorado River (10%) Owen's River aqueduct from Mammouth Lake (77.7%)	+	
Memphis, Tenn.	Artesian well	—	
Mobile, Ala.	Reservoir	+	1
Nashville, Tenn.	Cumberland River	+	
New Orleans, La.	Mississippi River	+	1
Riverside, Ill.	Chicago water supply and 2 wells	+	
San Francisco, Cal.	Hetchy Reservoir	+	10
Washington, DC	Potomac River	+	
Surface water			
Barataria Bay, La.			20
Gulf of Mexico*			200
Little Dauphin Island Bay, Ala.			20
Mississippi River (surface levels)			130
Mississippi River (deep levels)			400
Mobile, Ala. (reservoir)			80

Samples were obtained between June and September 1972.
* Gulf of Mexico sample obtained off Grant Isle, La.

cola drinks, and wine as negative, one brand of local commercial bottled water as positive, another brand derived from a 610-M (2000-ft) deep artesian well as negative, and milk at 30 to 130 μg/ml which rose sixteen-fold after 24 hours at room temperature but which showed no rise when refrigerated. The authors predicted value in use of the procedure for monitoring water, milk and other beverages, and biological solutions.

Jorgensen, Lee, and Pahren (10) applied the LAL procedure to drinking waters and to AWT effluents. Their tabular results are also reproduced herein, drinking water samples in Table 2, and AWT water samples in Table 3. Sodium thiosulfate was not added to any of the drinking water samples. The lowest endotoxin activity shown for drinking water samples is from Miami which also was the only ground water supply sampled.

All AWT samples were frozen prior to mailing. The only AWT samples in Table 3 free of endotoxin are from Escondido which uses reverse osmosis as a final treatment. Blue Plains uses breakpoint chlorination following GAC filtration and had relatively low endotoxin levels. Samples from Pomona treated by ozone did not differ substantially from samples treated by "normal" chlorination. The highest endotoxin-containing samples -- both from the Lake Tahoe plant -- were mailed to Cincinnati instead of to San Antonio and because of the lengthy time in transit getting to the proper lab, the results are not comparable with the other sample results.

The authors described variability in the potency of the amebocyte lysate preparation, problems of sample shipment, failure to perform bacteria plate counts, and failure to discriminate between bound and free endotoxin as their greatest shortcomings. Bound endotoxin is described as endotoxin remaining in association with the cell wall of viable bacteria, and free endotoxin is endotoxin that has been solubilized without autolysis or disruption of the cells. Further, the authors state that bound endotoxin can be used as a means of quantifying the number of bacteria present. A linear relationship exists between the number of cells and bound endotoxin over the range 10^3 to 10^6 bacteria per ml. Two of the most recent papers published utilize endotoxin methods to describe biomass and bacterial counts (11,12).

The study reported herein attempts to fill in some of the shortcomings while striving for additional objectives, viz:

1) To quantify pyrogenic activity of waters following GAC filtration in terms of capacity to initiate a fever via injection, ingestion, and inhalation in experimental animals, and

2) To observe the relationships of pyrogenicity with bacterial counts and the endotoxin assay.

3) To determine the effects of treatments on the pyrogenic or endotoxin results and