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Research and Development

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Project Summary

Determining the Effectiveness of an Afterburner to Reduce Dioxins and Furans

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During reactivation of granular activated carbon (GAC) used in the treatment of municipal water supplies, a potential exists for the release of adsorbed organic compounds or their reaction products into the environment. Combustion is normally emploved to reduce or eliminate trace organics from these types of effluent streams. The purpose of this study was to evaluate the effectiveness of an afterburner in reducing or eliminating the occurrence of dioxins and furans in the reactivator effluent streams. Quantitative measurements were made of tetrachlorodibenzo-p-dioxins (TCDDs) and tetrachlorodibenzofurans (TCDFs) in all effluent streams from the Cincinnati (Ohio) Waterworks reactivator unit and penta-, hexa-, hepta-, and octachlorinated dioxins (CDDs) and furans (CDFs) in a preselected number of samples.

Seven tests were performed to determine TCDD and TCDF emissions from the Cincinnati Waterworks carbon reactivation unit. The test sequence and sampling matrix is shown in Table 1. The tests were conducted during reactivation of a batch of carbon that had been used to adsorb trace organics from Cincinnati municipal drinking water. During Tests No. 1 and 7, the natural gas and fuel oil supplies used to fire the fluidized-bed reactivation system were sampled to determine if polychlorinated biphyenyls (PCBs) were present. The effluent streams along with reactivated and spent carbon feed samples were analyzed to determine (1) 2,3,7,8-TCDD and 2,3,7,8-TCDF concentrations; (2) total TCDD and TCDF

concentrations; and (3) the TCDD and TCDF isomeric composition, i.e., the number and, when possible, the identity of isomers in the sample. A selected number of samples were analyzed for the higher homologues of dioxins and furans.

This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Activated carbon has been used for many years to remove taste and odor components from drinking water. More recently, studies have focused on activated carbon treatment to remove potentially hazardous trace organics from municipal water supplies. In this regard, the Cincinnati Waterworks (CWW), in conjunction with the U.S. Environmental Protection Agency (EPA), has been conducting a study on the effectiveness of granular activated carbon (GAC) for removing these compounds from drinking water. Carbon used for water treatment can be thermally reactivated in a fluidized-bed furnace and reused in the water treatment process. During carbon reactivation, organic compounds could be released into effluent streams that will enter the environment. A part of the total evaluation of the net gains achieved by removing trace organics from water must include an examination of the potential for causing exposure to the public via alternative path-

Table 1. Test Sequence and Sampling Matrix for Cincinnati Waterworks Carbon Reactivator Tests

Process Streams to be Sampled (b)	Process	Streams	to be	Sampled(b)
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Test Sequence	Reactivator Fuel ^(a)	Afterburner Off/On	GAC Feed	Spent GAC	Regen. GAC	Scrubber Water	Carbon Fines	AB ^(c) 1 sec	AB ^(c) 2 sec	Recup. Inlet	Stack ^(c)	Fuel Supply
1	NG	Off	No		<u> </u>	X				TP		P
2	NG	Off	Yes	X	X	X	Τ			T		
3	NG	On	Yes	X	X	Τ	X		T		Τ	X
4	NG	On	Yes	X	X	X	X	T				
5	NG	On	Yes	ΤP	TP	TP	X		TP		ΤP	X
6	NG	Off	Yes	X	X	X	TP			TP		X
7	FO	Off	No			X				T		P
No. Sample To be Analy				1	1	2	2	2	4	8	4	2

a) NG - Natural Gas, FO - Fuel oil.

ways. Substances removed from the water must be properly handled regardless of the treatment methodology used.

During August and September 1982, a study was performed by Battelle's Columbus Laboratories (BCL) to measure TCDDs and TCDFs in the effluent streams of the CWW carbon reactivator. Since this work, the reactivation system has been modified by incorporating an afterburner in the off-gas streams from the fluidized-bed reactivation unit. The purpose of the afterburner is to destroy organic compounds in the off-gas stream by thermal decomposition and, thus, minimize their release into the environment.

The purpose of this second study was to evaluate the effectiveness of the afterburner unit in reducing or eliminating the occurrence of dioxins and furans in the reactivator effluent streams and to determine quantitatively TCDDs and TCDFs in all effluent streams from the Cincinnati Waterworks reactivator unit during a carbon reactivation cycle. The possible presence of TCDDs and TCDFs in the spent carbon feedstock and PCBs in the fuel gas supply used to fire the reactivator were also evaluated.

Seven tests were performed to measure TCDD and TCDF levels in the effluent streams and the spent carbon feedstock of the Cincinnati Waterworks carbon reactivation system (shown schematically in Figure 1). The tests

During each test, samples were acquired from the process streams identified in Figure 1. The stack, afterburner, and recuperator effluent streams were sampled with an EPA Method 5 train that had been modified by adding a water-cooled condenser and 22-g XAD-2* trap between the filter and first impinger to collect TCDDs and TCDFs in the vapor phase of the sample stream. Gas temperature at the exit of the XAD-2 trap was maintained at <20°C (<68°F). Grab and composite procedures were used to collect samples of the dryer off-gas cyclone catch, scrubber water, reactivated carbon, and spent carbon feed. During two of the tests, the natural gas and fuel oil were sampled (XAD-2 trap for the natural gas and grab sample for the fuel oil) to determine if PCBs were present in the fuel supply used to fire the carbon reactivation system.

TCDD and TCDF analyses of the effluent and spent carbon feed samples were performed by (1) either Soxhlet or liquid-liquid extraction to remove the analytes from the sample matrix and (2) removal of co-extracted interferences with silica liquid chromatographic columns, TCDD and TCDD isomers were identified and quantitated by combined high resolution gas chro-

matography/high resolution mass spectrometry (HRGC/HRMS). PCB analyses were performed by (1) Soxhlet extraction of the XAD-2 and (2) concentration of the extract. PCBs were determined by combined HRGC/MS.

Results

No 2,3,7,8-TCDD was detected in any emission or process streams. TCDD was not detected in any stack particulate samples; however, small concentrations were detected in the vapor phase (XAD-2) of the afterburner and recuperator. Low concentrations were also found in one cyclone catch sample. Octa-CDD was detected in all emission and process streams, ranging from 3.123 ng/dry standard cubic meter (dscm) (0.153 ppt) in recuperator particulates to 0.15 ng/g (0.007 ppt) in the spent GAC. Hepta-CDD was detected in all emission streams, ranging from 0.27 ng/dscm (0.014 ppt) in the afterburner particulates to 0.024 ng/dscm (0.001 ppt) in the vapor phase of the afterburner. Trace amounts of the hepta-CDD were also detected in one spent GAC sample. Penta- and hexa-CDD were detected in the vapor phase of the recuperator. The values were 0.128 ng/dscm (0.008 ppt) and 0.372 ng/ dcsm (0.021 ppt), respectively. Trace amounts of hexa-CDD were also detected in the cyclone catch.

No 2,3,7,8-TCDF was detected in the particulate phase of any emission stream; however, trace amounts were found in the gas phase of all emission streams. Low concentrations were also observed in one cyclone catch sample. TCDF was found in recuperator emis-

1Howes, J. E., Jr., DeRoos, F. L., Aichele, D., Kohler,

b) X - Sample collected and archived.

T - Sample collected and analyzed for TCDD/TCDF only.

TP - Sample collected and analyzed for TCDD/TCDF and PCDD/PCDF.

P - Sample collected and analyzed for PCB.

c) Modified Method 5 train with a sorbent (XAD-2) used for each test.

were conducted during reactivation of an approximately 40,000-lb batch of GAC, which had been used in a contactor for approximately 200 days to treat Cincinnati municipal water.

^{*}Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

D. F., and Larson, M. E. "Determination of Dioxin Levels in Carbon Reactivation Process Effluent Streams." Final Report on EPA Contract No. 68-02-3487, Work Assignment No. 16, May 1983.

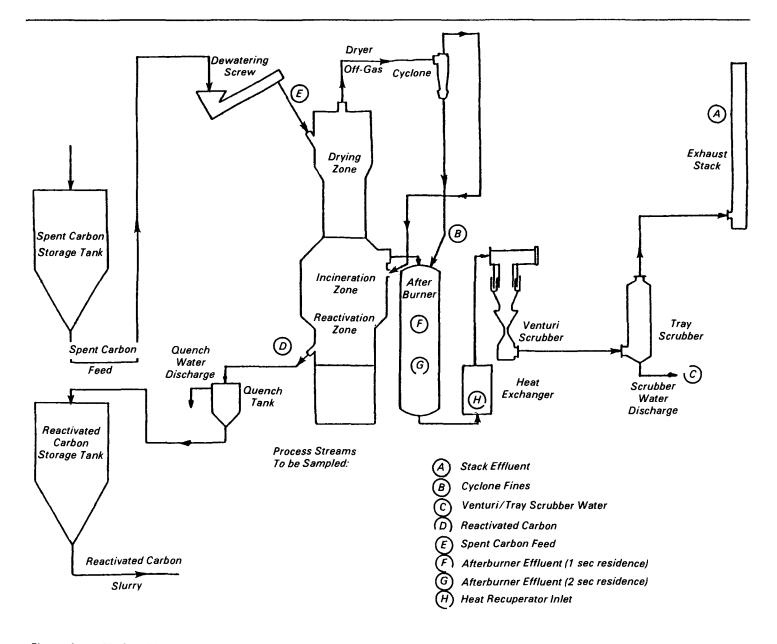


Figure 1. Cincinnati Waterworks carbon reactivation system.

sions (particulate and gaseous) and in the gaseous phase of the afterburner and stack. The range was from 0.01 ng/dscm (0.0007 ppt) in recuperator particulate to 1.357 ng/dscm (0.10 ppt) in the vapor phase of the recuperator. TCDF was also observed in the cyclone catch and in the spent GAC. Penta-CDF was detected in emissions (gaseous and particulates) from the afterburner and recuperator. None were detected in stack emissions. The range was 1.067 ng/dscm (0.071 ppt) in the gaseous phase of the recuperator, to 0.015 ng/dscm (0.001 ppt) in the particulate

phase of the afterburner. No penta-CDF was found in any of the process samples. Hexa-CDF was detected in the vapor phase of the recuperator and afterburner and in the particulate phase of the afterburner and stack. The range was 0.756 ng/dscm (0.046 ppt) in the vapor phase of the recuperator to 0.007 ng/dscm (0.0004 ppt) in the vapor phase of the afterburner.

Trace amounts of the hexa-CDF were also found in the cyclone catch. Hepta-CDF was detected in the vapor phase of the recuperator and afterburner and in the particulate phase of the afterburner

and stack. The range was 0.756 ng/dscm (0.046 ppt) in the vapor phase of the recuperator to 0.018 ng/dscm (0.001 ppt) in the vapor phase of the afterburner. Trace amounts of the hepta-CDF were found in the spent GAC. Octa-CDF was detected in the vapor phase of the recuperator and afterburner and in the particulate phase of all emission streams. The range was 0.368 ng/dscm (0.018 ppt) in the particulate phase of the recuperator to 0.012 ng/dscm (0.0006 ppt) in the vapor phase of the afterburner. No octa-CDF was detected in any process samples.

Only one PCB isomer was detected in the natural gas supply and none in the fuel oil. The monochlorobiphenyl (Cl₁) detected in the natural gas was $0.71 \mu g/s$ sample (0.056 ppb by volume). The detection limit of the monochlorobiphenyl is $0.18 \mu g/s$ ample.

Reactivated carbon and spent carbon samples obtained during the test program and a sample of virgin carbon of the type being reactivated were analyzed for total organic halogens (TOX). The TOX levels found in the samples were: virgin carbon, <50 mg/Kg; reactivated carbon, <50 mg/Kg; and spent carbon, 416.3 mg/Kg.

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Ben W. Lykins, Jr. is the EPA Project Officer (see below).

The complete report, entitled "Determining the Effectiveness of an Afterburner to Reduce Dioxins and Furans," (Order No. PB 86-175 718/AS; Cost: \$16.95, subject to change) will be available only from:

National Technical Information Service 5285 Port Royal Road Springfield, VA 22161 Telephone: 703-487-4650

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