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Project Summary

Emissions of Metals, Chromium and Nickel Species, and Organics from Municipal Wastewater Sludge Incinerators

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In order to provide data to support regulations on municipal wastewater sludge incineration, emissions of metals, hexavalent chromium, nickel subsulfide, polychlorinated dibenzo-dioxins and furans (PCDD/PCDFs), semivolatile and volatile organic compounds, carbon monoxide (CO), and total hydrocarbons (THCs) from two multiple hearth incinerators and a fluidized bed incinerator were measured. The emissions were controlled at each unit with venturi/scrubbers and, on two of the units, emissions from wet ESPs were determined. Flue gas sampling was conducted at the inlet and outlet of the air pollution control devices. Feed sludge was tested for metals, moisture, and carbon and hydrogen content. Testing occurred at both normal and improved (low CO) combustion conditions. Two additional tests were conducted under this study to evaluate draft methods for sampling and analysis of hexavalent chromium and systems for continuous monitoring of CO and THC emissions.

All test results are fully documented in individual site reports. Emission test results are separated into normal and low CO conditions. Gas concentrations, mass emission rates, metals-to-particulate ratios, and emissions factors are presented. The ratios of hexavalent-to-total chromium and nickel subsulfide-to-total nickel are given. Analytical results for the process samples are provided. Isomer-specific PCDD/PCDF and semivolatile and volatile organic compound concentrations are reported. Continuous emission monitoring results for SO_2, NO_x, CO_2, O_2, CO, and THC are presented.

This Project Summary was developed by EPA's Risk Reduction Engineering 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

The U.S. Environmental Protection Agency's (EPA's) Office of Water (OW) has been developing new regulations for sewage sludge incinerators and EPA's Risk Reduction Engineering Laboratory (RREL) has been assisting OW collect supporting data. There is particular concern regarding chromium and nickel species in the emissions from incineration of municipal wastewater sludge because of the associated cancer risk. OW has drafted risk-based sludge regulations under Section 405d of the Clean Water Act that have been published for comment in the *Federal Register*, Volume 54, No. 23, February 6, 1989. Final regulations are scheduled for publication in the *Federal Register* in July 1992.

The draft regulations are based on the risk incurred by the "most exposed individual" (MEI). The MEI approach involves calculating the risk associated with an individual residing for 70 yr at the point of maximum ground level concentration of the emissions just outside the incinerator facility property line. EPA's proposal for regulating sewage sludge incinerators is based on ensuring that the increased ambient air concentrations of metal pollutants emitted from sludge incinerators are below the am-

bient air human health criteria. The concentrations are identified in the proposed regulations as Risk Specific Concentrations (RSCs). Both nickel and chromium emissions from sludge incinerators presented a specific problem in establishing RSCs, because unknown portions of the emissions of these metals are in forms that are harmful to human health. In performing the risk calculations, EPA assumed that 1% of the emissions of chromium from the sludge incinerators is in the most toxic form, hexavalent chromium. This was based on limited data. For nickel, EPA assumed that 100% of the nickel emissions are in the most toxic form, nickel subsulfide. No data on nickel subsulfide were available so the most conservative approach was taken. The lack of a substantial data base on hexavalent chromium and nickel subsulfide prompted EPA to plan additional measurements of these constituents in sewage sludge incinerator emissions.

To collect additional data, a comprehensive test program was developed to determine the ratios of hexavalent-to-total chromium and nickel subsulfide-to-total nickel for a typical sewage sludge incinerator under normal combustion conditions (higher concentrations of carbon monoxide and total hydrocarbons) and improved combustion conditions (lower concentrations of carbon monoxide and total hydrocarbons).

Test Methods

At Site 5 (continuing a numbering system initiated in a previous 4-site project) tests were only conducted for methods development purposes. At Site 6, emissions were measured at the inlet and outlet of the control device. At Site 7, an evaluation of CO and THC continuous emission monitoring systems (CEMSs) was performed. At Sites 8 and 9, emissions were measured at the inlet of the venturi scrubber, at the midpoint located between the venturi scrubber and the wet ESP, and at the outlet of the wet ESP. For Sites 6, 8, and 9, midpoint and outlet air emission samples were collected and analyzed for particulate matter, metals, PCDD/PCDFs, volatile and semivolatile compounds (except Site 6), and hexavalent chromium and nickel subsulfide species. Continuous emission monitoring (CEM) for O_2, CO_2, CO, SO_2, and NO_x at the control system inlet and O_2 (except Site 6), CO_2 (except Sites 6 and 9), CO, SO_2 (except Sites 6 and 9), NO_x (except Sites 6 and 9), and THC was conducted at the control system outlet stack. The monitoring data were used principally to determine process and control equipment operating conditions during the chromium and nickel speciation tests. Process samples consisting of sludge feed, scrubber inlet and discharge water, and bottom ash (except Site 8) were collected. Process samples were analyzed for the metals listed in Table 2 and were subjected to ultimate and proximate analysis. The heating value of the sludge feed was calculated from the carbon and hydrogen content.

Particulate matter and metals sampling was conducted following the procedures in the draft EPA method, "Methodology for the Determination of Trace Metals Emissions in Exhaust Gases from Stationary Source Combustion Processes."

Flue gas sampling for PCDD/PCDFs and semivolatile organic compounds followed procedures in SW-846 Method 0010, except that a final toluene rinse was conducted and analyzed separately for PCDD/PCDF. The samples were analyzed for PCDD/PCDF using SW-846 Method 8290 and for other semivolatile organic compounds using a combination of SW-846 Methods 3540, 3550, 3510, 3520, and 8270.

Flue gas sampling for volatile organic compounds employed the volatile organic sampling train (VOST) in accordance with SW-846 Method 0030.

Flue gas sampling and analysis for hexavalent chromium followed the procedures in the draft EPA method, "Determination of Hexavalent Chromium from Stationary Sources." This sampling train continuously recirculates the impinger solution to the sample nozzle to prevent conversion of hexavalent chromium during sampling. A radioactive hexavalent chromium isotope was used to verify that conversion was not significant. Hexavalent chromium samples were analyzed by ion chromatography coupled to a diphenylhydrazine post-column reaction (IC/PCR) on the filtered impinger samples. Diphenylhydrazine complexes of tri- and hexavalent chromium were analyzed colorimetrically.

Flue gas sampling and analysis for nickel species followed the draft EPA method, "Methodology for the Determination of Nickel Compound Emissions from Stationary Sources." Analysis of the nickel speciation samples was performed following the Nickel Producers Environmental Association (NiPERA) sequential leaching method. The ratios of sulfidic nickel species, nickel subsulfide (Ni_3S_2) and nickel sulfide (NiS), to total Ni were determined.

EPA Methods 1, 2, 3, and 4 were used in conjunction with the sampling procedures described above. Method 3 samples were collected as backup for O_2 and CO_2 determination should the CEMSs data be unavailable.

The CEMSs used to measure concentrations of CO, CO_2, O_2, NO_x, SO_2, total hydrocarbons (THC as propane) followed the EPA instrumental Methods 10, 3A, 7E, 6C, and 25A, respectively. The primary intent of the continuous monitoring effort was to: (1) determine concentrations of these compounds and (2) provide a real-time indication of combustion conditions. The continuous monitoring systems were calibrated daily, but no attempt was made to certify the monitors using the EPA instrumental test methods.

The dewatered sludge samples were analyzed for the target metals after determination of their moisture and ash content, heating value, and proximate and ultimate analyses.

Incinerator and control system operating parameters were monitored during all manual test runs to characterize the system operations.

Results

The metals found in the greatest concentration in the sludge were lead, chromium and nickel. The particulate matter and metals emissions factors from the normal control device (venturi/scrubber) outlet are shown for normal and low CO conditions (Table 1). At Sites 6, 8, and 9, the metals were measured at the venturi/scrubber inlet and outlet, and for Sites 8 and 9, at the outlet of the wet ESP. The removal efficiencies were calculated and are summarized in Table 2.

The need for sampling hexavalent chromium without artifact formation and analysis of the resulting samples specifically for hexavalent chromium at low concentrations was a major accomplishment of this test program. Sampling activities conducted at Site 5 were dedicated to developing a suitable measurement method for hexavalent chromium in emissions from incineration of municipal wastewater sludge. Hexavalent chromium sampling at the venturi/scrubber outlets at Sites 6, 8, and 9 followed the same procedures of the draft EPA method. The surrogate recoveries for Sites 6, 8, and 9 at both midpoint and wet ESP outlets are shown in Table 3, along with the ratio of hexavalent to total chromium measured with the recirculation train. At Site 6, the hexavalent to total chromium ratio increased from 1.9% to 8.3% between the normal combustion conditions to the low CO (improved combustion) conditions. This observation, shown graphically in Figure 1, can be explained by the higher hearth temperatures and excess oxygen levels recorded during the improved combustion condition that would favor the formation of hexavalent chromium. At Site 8, a fluidized bed incinerator, the hexavalent chromium to total chromium ratio was below the detection limit (<2%) at both the scrubber and wet ESP outlets. At Site 9, a multiple hearth

Table 1. *Particulate and Metals Stack Emission Factors for Steady State (Low CO) and Normal Operation*

	Emission Factors (g metal emitted/g metal fed)				
Pollutant	Site 6 Normal	Site 6 Low CO	Site 8 Normal	Site 9 Normal	Site 9 Low CO
PM (g/kg dry sludge feed)	0.37	0.45	4.59	0.36	0.04
Arsenic	ND[a]	ND	ND	<0.011[b]	<0.013
Beryllium	<0.069	0.059	<0.0001	ND	ND
Cadmium	0.917	0.908	0.0003	0.336	<0.008
Chromium	0.011	0.005	0.0001	0.036	0.001
Lead	0.123	0.136	<0.0001	0.101	0.006
Nickel	0.030	0.013	<0.0001	0.004	0.0004

[a]ND - Not detected, all sample measurements were below the analytical detection limit.
[b] < - Outlet samples were below analytical detection limit, calculated ratio is less than value shown.

Table 2. *Metals and Particulate Removal Efficiency Across the Various Control Devices (%)*

Element	Site 6 Normal Scrubber	Site 6 Low CO Scrubber	Site 8 Normal Scrubber	Site 8 Normal Wet ESP	Site 9 Normal Scrubber	Site 9 Low CO Scrubber	Site 9 Low CO Wet ESP
Arsenic	NA[a]	NA	>99.5	NA	NA	NA	NA
Beryllium	>85.5	>86.7	>99.95	NA	--	--	--
Cadmium	71.9	77.3	99.82	71.0	0.0	45.0	>98.0
Chromium	99.3	99.4	99.92	62.0	0.0	89.0	88.0
Lead	71.3	78.1	99.91	>96.0	5.0	54.0	96.0
Nickel	93.4	94.5	99.89	81.0	89.0	96.0	90.0
Particulate Matter	98.5	97.6	99.99	78.0	85.0	95.0	87.0

[a]NA - Not applicalbe.

Table 3. *Hexavalent Chromium Sampling Results*

	Site 6 Normal %	Site 6 Low CO %	Site 8 Normal %	Site 9 Normal %	Site 9 Low CO %
Venturi/Scrubber Outlet					
Surrogate recovery	90.5	95.6	66.8	84.3	90.5
Hexavalent to total Cr ratio	1.9	8.3	<1.8	11.9	7.9
Wet ESP Outlet					
Surrogate recovery	NA[a]	NA	81.5	90.1	93.1
Hexavalent to total Cr ratio	NA	NA	<1.4	29.9	42.5

[a]NA - Not applicable.

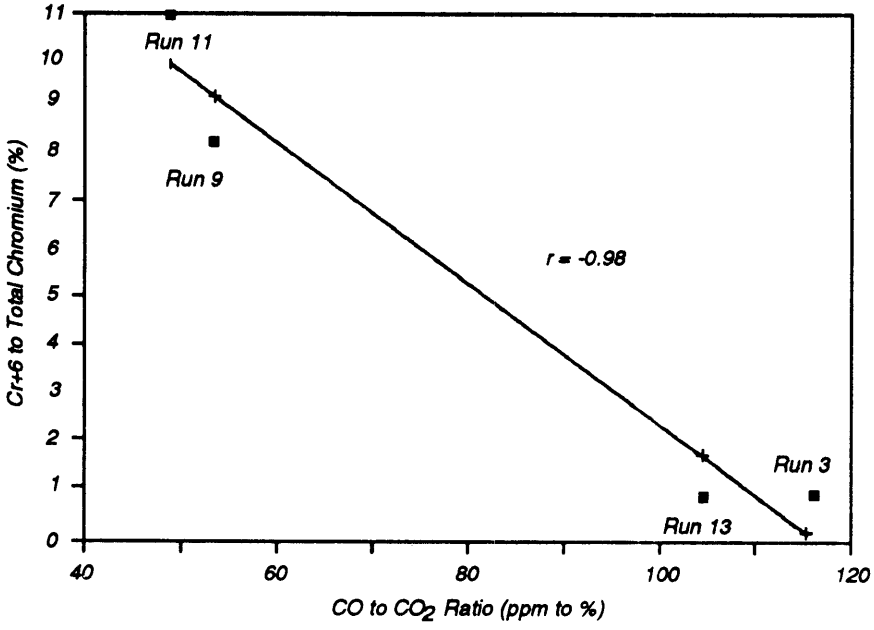

Figure 1. Correlation of combustion efficiency and hexavalent to total chromium ratio of Site 6.

furnace, the hexavalent to total chromium ratio increased from 11.9% to 29.9% between the normal combustion conditions to the low CO (improved combustion) at the scrubber outlet and increased from 29.9% to 42.5% at the wet ESP outlet. The increased percentage of hexavalent chromium at the wet ESP outlet is a result of higher collection efficiency of trivalent chromium by the wet ESP.

The results of the nickel sampling and analysis indicate that within the detection limit of the wet chemical method, no nickel subsulfide was present in the air emissions.

Sampling for PCDD/PCDFs was performed at the venturi/scrubber outlet at Sites 8 and 9 (termed the Midpoint at Site 9) and at the wet ESP outlet at Site 9. Sampling at Site 9 was conducted at both normal and low CO conditions. The results for the PCDD/PCDF sampling are shown in Table 4.

At Site 9, sampling for semivolatile organic compounds was performed at the venturi/scrubber outlet (Midpoint) and the wet ESP outlet under both normal and low CO conditions. The results for the semivolatile organic compound sampling are shown in Table 5. The concentration of the volatile organics in the flue gas are presented in Table 6.

At Sites 6 and 9, a positive correlation between carbon monoxide emissions and THC emissions was observed. At Site 8, both the CO and THC emissions were sufficiently low that a correlation could not be seen.

At Site 7, positive correlations were demonstrated for the "Hot" and "Cold" THC CEMs.

The accomplishments of the study were far greater than could have been anticipated at the outset of the program. Specifically, the following has been accomplished.

(1) Documented hexavalent chromium emissions from sewage sludge incinerators.
(2) Documented nickel subsulfide emissions from sewage sludge incinerators.
(3) Developed a hexavalent chromium sampling and analytical method.
(4) Developed a nickel speciation sampling and analytical method.
(5) Provided additional metals data.
(6) Provided additional trace organics data.
(7) Documented a correlation between CO and THC.
(8) Documented that CO and THC concentrations can be reduced when the plant has a CO and/or THC monitor to improve combustion conditions.
(9) Demonstrated that the use of a wet ESP is a viable retrofit option for significantly reducing particulate and metals emissions.

The full reports were submitted in fulfillment of Contract No. 68-CO-0027 under the sponsorship of the U.S. Environmental Protection Agency.

Table 4. Dioxin/Furans Emissions Summary

	Concentration (ng/DSCM				
Congeners	Site 8 Normal Outlet	Site 9 Normal Outlet	Site 9 Normal Mid-Point	Site 9 Low CO Outlet	Site 9 Low CO Mid-Point
Total Tetra-Octa CDD	0.721	3.2	20.2	0.7	1.6
Total Tetra-Octa CDF	1.41	12.4	81.9	2.1	7.1
Total Tetra-Octa CDD/CDF	2.13	15.6	102	2.8	8.7

Table 5. Semivolatile Emissions Summary for Outlet and Midpoint at Site 9

Analyte	Concentration (µg/DSCM[a])			
	OUT-MM5-7A	MID-MM5-7	OUT-MM5-7C	MID-MM5-7C
Phenol	ND[a]	ND	176	162
1,4-Dichlorobenzene	30.8	33.4	ND	ND
Benzyl alcohol	800	1120	4100	3930
1,2-Dichlorobenzene	25.6	26.7	ND	ND
4-Methylphenol	ND	ND	21.2	20.6
2-Nitrophenol	196	284	43.1	76.4
Benzoic acid	2850	3220	5090	4240
1,2,4-Trichlorobenzene	699	768	ND	ND
Naphthalene	976	864	ND	ND
4-Chloroaniline	ND	ND	ND	ND
2-Methylnaphthalene	43.4	45.5	ND	ND
4-Nitrophenol	ND	ND	97.4	1440
Dibenzofuran	45.2	44.7	ND	ND
Phenanthrene	44.9	33.4	13.7	ND
Fluoranthene	ND	13.3	ND	ND
bis (2-Ethylhexyl)phthalate	29.2	26.1	ND	71.6

[a] = 68°F -- 29.92 inches Hg.
[b]ND = Not detected; used as zero (0)

Table 6. Volatile Organics Emissions Summary

	Concentration, µg/DSCM[a]	
	Site 8 Venturi/Scrubber Outlet	Site 9 Wet ESP Outlet
Acrylonitrile	ND[b]	1060
Vinyl Chloride	ND	66.2
Methylene Chloride (m/z = 86)	108	38.3
Chloroform	16.8	24.1
1.2-Dichloroethane	ND	ND
1,1,1-Trichloroethane	6.8	17.5
Carbon Tetrachloride	ND	ND
Trichloroethene	5.2	24.6
Benzene	6.2	6390
Tetrachloroethene	9.4	29.0
Toluene	7.7	4080
Chlorobenzene	ND	55.5
Ethylbenzene	2.6	100

[a] = 68°F -- 29.92 inches Hg.
[b]ND = Reported as not detected or estimated values; both expressed as zero (0) in calculating totals and averages.

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he complete report consists of nine volumes entitled "Emissions of Metals, Chromium and Nickel Species, and Organics from Municipal Wastewater Sludge Incinerators," Set Order No. PB92-151 547; Cost: $232.00, subject to change).

"Volume I. Summary Report ," (Order No. PB 92-151 554; Cost: $19.00, subject to change).

"Volume II. Site 5 Test Report - Hexavalent Chromium Method Evaluation ," (Order No. PB 92-151 562; Cost : $19.00, subject to change).

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