



# Mercury Impacts on By-Products

DOE NETL Mercury Control  
Project Review Meeting  
July 14–15, 2004



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University of North Dakota  
Energy & Environmental Research Center

# Project Partners

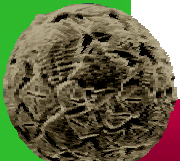
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## Sponsors

- Cinergy
- EERC Center for Air Toxic Metals Affiliates
- EPRI
- Great River Energy
- North Dakota Lignite Research Council
- U.S. Department of Energy National Energy Technology Laboratory
- Utility Solid Waste Activities Group

## Research Team

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- David J. Hassett
- Loreal V. Heebink
- John R. Gallagher
- Dennis L. Laudal
- John H. Pavlish



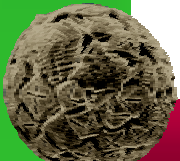
# Project Objectives

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*Evaluate the impact of mercury and other air toxic elements on the management of coal combustion byproducts (CCBs).*

Supporting objectives:

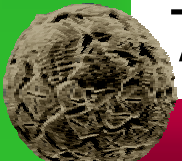
- 1) Determine the release potential of selected air toxic elements.
- 2) Increase information on Hg/ATE releases for CCBs.
- 3) Develop comparative laboratory and field data.
- 4) Establish appropriate laboratory and field protocols.



# Project Tasks

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1. Literature Search
2. **Analytical Methods Selection**
3. **Sample Identification and Selection**
4. **Chemical and Physical Characterization**
5. **Laboratory Evaluation of Air Toxic Element Releases**
  - Leaching
  - Vapor Transport
  - Microbiological Release
6. Field Investigations
7. Data Reduction and Interpretation





# Methods Development and Selection – Status



# Leaching

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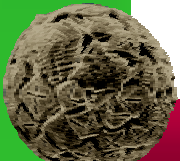
- DOE NETL interlaboratory study
- Synthetic groundwater leaching procedure (SGLP) with long-term leaching (LTL)
- Toxicity characteristic leaching procedure (TCLP)



# Vapor Transport

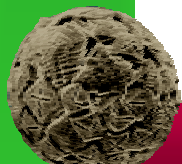
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- Long-term ambient temperature desorption
- Elevated temperature thermal devolatilization
- Microbiologically mediated release



# Long-Term Ambient Temperature

- 2 week blanking for sample containers
- Hg-free air used
- Hg exiting the sample containers is trapped and quantitated



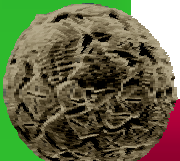
# Thermal Release

- Approximately 1 gram of sample is used.
- Sample is heated from ambient temperature to 700°C at 25°C/min.
- Mercury release is measured in real time.
- Improved reproducibility and quantitation achieved using mass flow controller.



# Microbiological Release

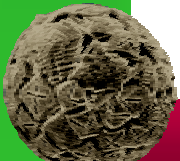
*Improved Apparatus*



# Microbiological Release

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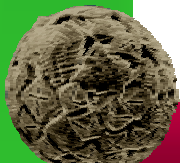
- Stirred, not shaken.
- Initiated sampling of leachate.
- Post-test bacterial counts performed.
- Initiated implementation of new methodology, SPME, for organo-mercury speciation.



# Solid-Phase Microextraction (SPME)

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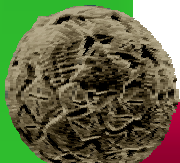
- Fiber is coated with 100  $\mu\text{m}$  of polydimethylsiloxane.
- Sample is derivatized with sodium tetraethylborate, tetrapropylborate, or tetraphenylborate.
- Fiber is exposed to headspace of heated sample.
- Fiber is inserted into a GC.



# What does SPME do?

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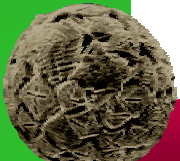
- Sampling of vapor from reaction vessel.
- Sampling of liquid samples.
- Determines methylmercuric chloride and dimethyl mercury as well as any other organomercury species.
- May determine elemental mercury and divalent mercury.



# GC Speciation

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- Separates organomercury compounds on a nonpolar stationary phase, using atomic fluorescence detection.
- Determines methylmercuric chloride and dimethyl mercury from microbiologically mediated release experiments.



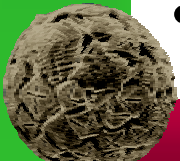
# Sample Identification and Selection – Status



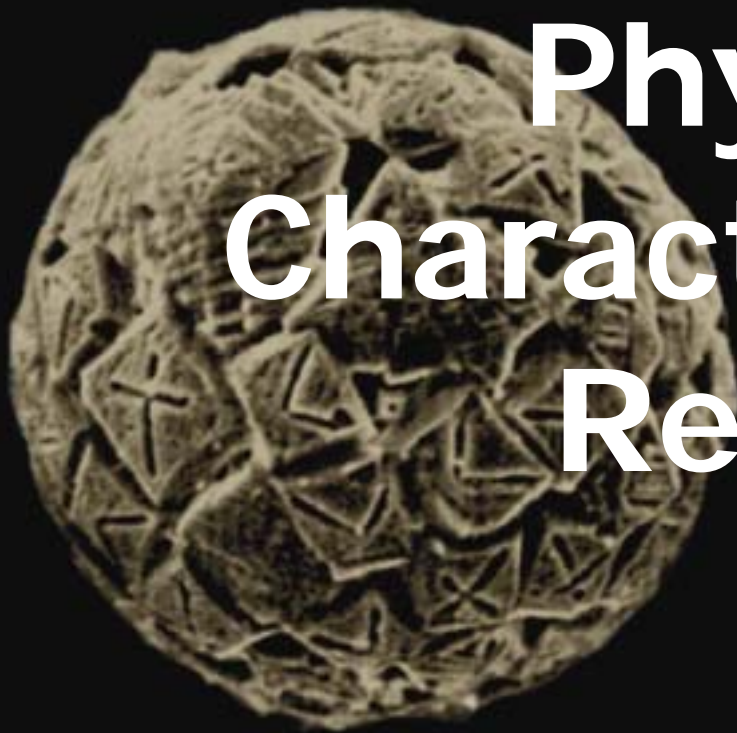
# Current Sample Set

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- 85 total samples
- Coal types
  - 18 lignite
  - 6 subbituminous
  - 61 bituminous
- Control technologies
  - 11 SO<sub>2</sub>
  - 11 NH<sub>3</sub>
  - 19 Hg
- Total mercury range <0.005–120 µg/g

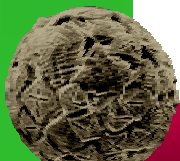


# Chemical and Physical Characterization Results



# Carbon Forms and Total Hg

Dominant Carbon Form	Number of samples evaluated	Range of Total Hg Content (ug/g)
Anisotropic Coke	7 samples	0.4–120
Isotropic Coke	4 samples	0.6–5.5
Unburned Coal	8 samples	0.005–0.5
Inertinite	3 samples	0.1–2.2
Vitrinite	4 samples	0.004–0.7



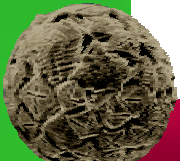


# Results of Release Experiments

# Procedures Completed To Date

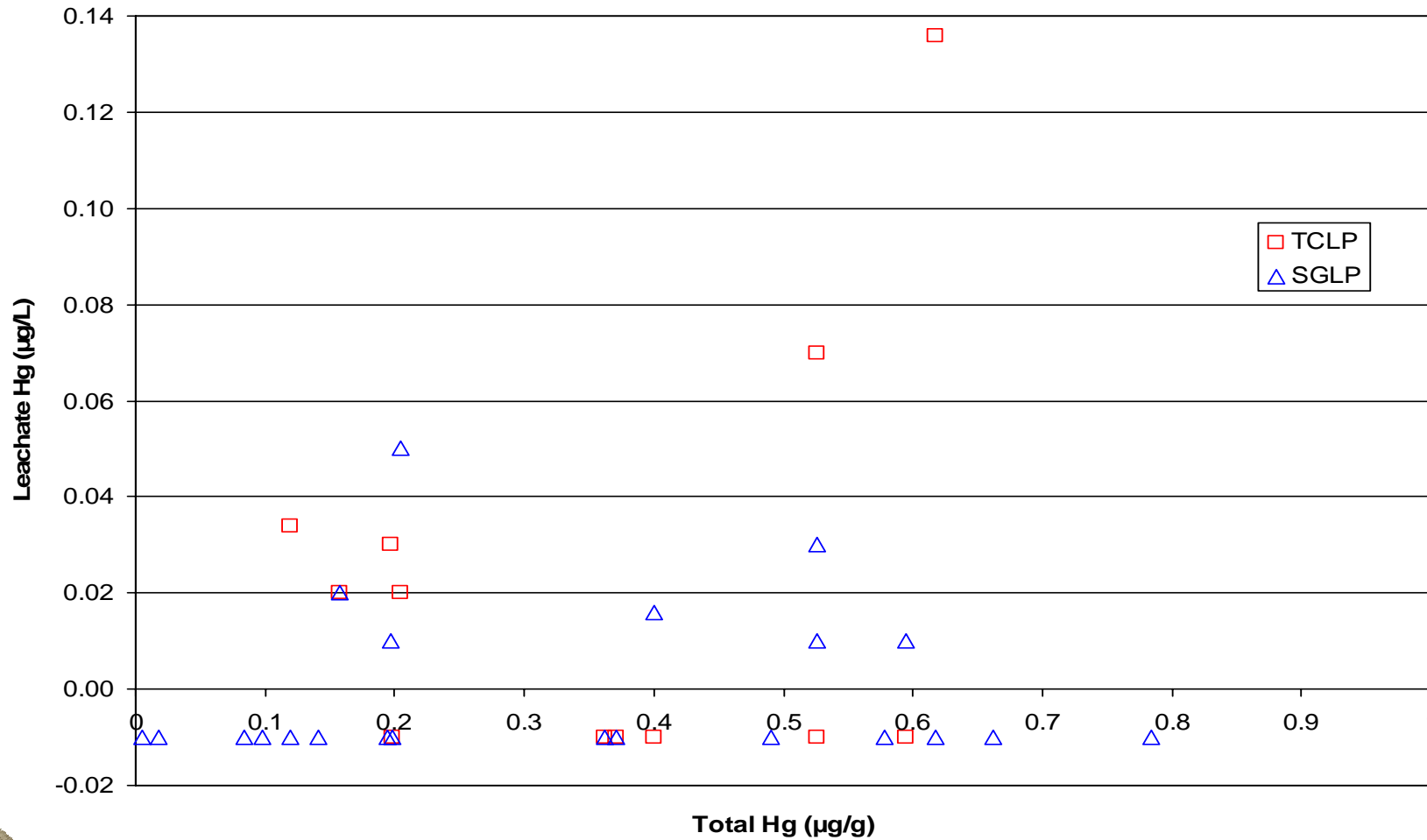
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- Start date April 1, 2003
- Toxicity characteristic leaching procedure (TCLP) on 20 samples
- Synthetic groundwater leaching procedure (SGLP) on 57 samples
- Long-term leaching (LTL)
  - 30-day on 13 samples
  - 60-day on 20 samples
- Thermal desorption of Hg on 12 samples
- Long-term ambient Hg release on 6 samples
- Microbiological Hg release on 1 sample

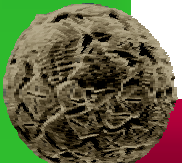




# Leachate vs. Total Hg (0–1 $\mu\text{g}/\text{g}$ ) – Year 1 Data



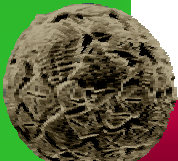
Non-detects are shown as negative values.



# Leachate Results, $\mu\text{g/L}$

## Summary of Data

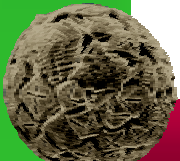
	Number of Samples	As	Cd	Cr	Pb	Hg	Ni	Se
<b>SGLP</b>	44	<2–266	<.02–8.08	<2–560	<2–14.3	<0.01–0.404	<2–60	<2–412
<b>30-Day</b>	2					<0.01		
<b>60-Day</b>	13	6.5–336	<0.2–7.22	<2–250	<2	<0.01–0.239	<2–70	22.7–514
<b>TCLP</b>	20					<0.01–0.136		



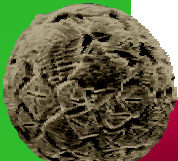
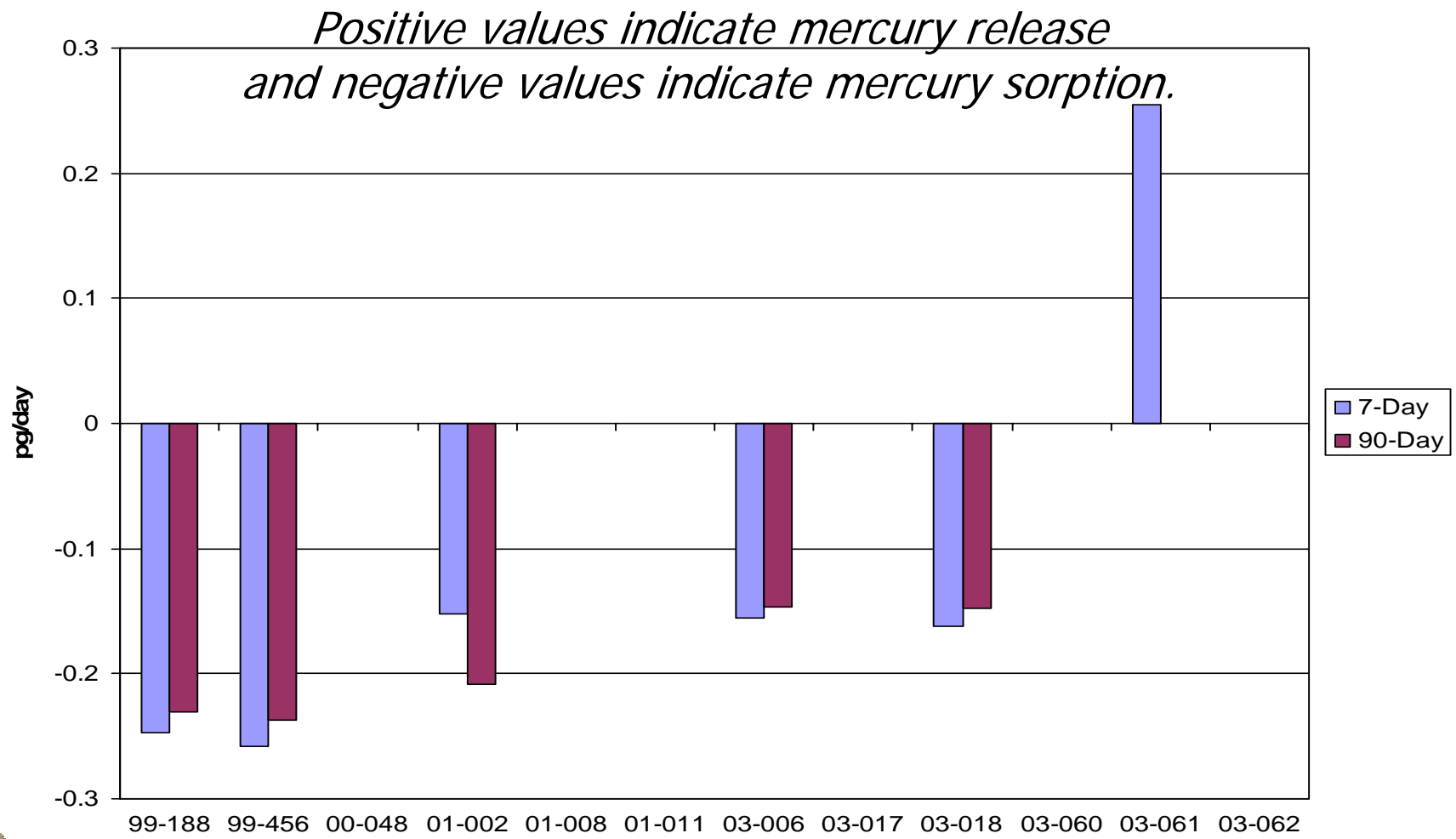
# Leaching

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- As, Cd, and Se typically leached at levels above detection limits.
- Cr & Hg leached at above detection limit  $\frac{1}{2}$  of the time.
- 22 out of 40 total samples exceeded 10 ppb for As.
- There was no correlation between total mercury and leachable mercury.



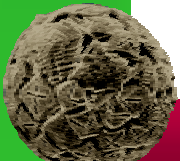
# Long-Term Ambient Temperature Release Results – Year 2



# Long-Term Ambient Temperature – Year 1 Conclusions

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- Five of six samples to date have acted as mercury sinks.
- The sixth sample was also likely a mercury sink. It is currently being reinvestigated.



# Thermal Release

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- One- or two-peak desorption peaks were the norm.
- Samples can be reproduced.
- Mercury generally released at temperatures greater than 200°C.
- Speciation has not been achieved.



# Microbiological Release (01-002)

<b>Anaerobic</b>	<b>Elemental Hg, pg/g</b>	<b>OrganoHg, pg/g</b>	<b>Bacterial Count, #/mL</b>
Fed	3.10	0.27	<30
Fed	3.55	0.28	<30
Fed	7.54	0.25	<30
Starved	1.33	0.26	<30
Starved	0.90	0.45	<30
Starved	1.13	0.40	<30
<b>Aerobic</b>			
Fed	8.11	0.28	>24,000,000
Fed	35.2	1.04	>24,000,000
Fed	2.72	0.26	>24,000,000
Starved	0.96	0.12	43,000
Starved	1.59	0.27	24,000
Starved	0.61	0.10	150,000



# Microbiological Release (03-060)

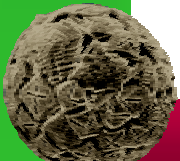
<b>Anaerobic</b>	<b>Elemental Hg, pg/g</b>	<b>OrganoHg, pg/g</b>	<b>Bacterial Count, #/mL</b>
Fed	2.42	0.28	>24,000,000
Fed	3.21	0.26	1,500,000
Fed	1.15	0.07	930,000
Starved	0.87	0.04	<30
Starved	0.75	0.03	40
Starved	1.72	0.07	40
<b>Aerobic</b>			
Fed	57.9	0.36	>24,000,000
Fed	22.8	0.62	>24,000,000
Fed	45.7	0.25	>24,000,000
Starved	0.85	0.09	4300
Starved	0.71	0.07	430
Starved	1.34	0.06	<30



# Microbiologically Mediated Vapor Phase Mercury Release

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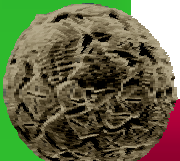
- Releases, while above non-microbiologically mediated releases, were low.
- There was evidence of methylation.



# Microbiologically Mediated Leaching

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- Organo-mercury compounds are present.
- Preliminary SPME results indicate presence of diethylmercury and dimethylmercury at ng/L levels ( $< 5$ ).



The image features two spherical wooden objects, possibly marbles or decorative spheres, with complex, interlocking geometric carvings. They are set against a black background. The sphere on the left is larger and more prominent, while the one on the right is smaller and positioned higher. The text 'Planned Activities' is overlaid in white, bold font across the center of the image. The overall design is framed by a green vertical bar on the left and a red horizontal bar at the bottom.

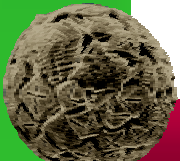
# Planned Activities

# Remaining Year 2 Plans

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## Laboratory

- Complete thermal desorption mercury and selenium curves on 15 samples.
- Continue LTL and SGLP experiments and analyze results.
- Continue ambient temperature mercury release experiments.
- Evaluate trace element analyses results.



# Remaining Year 2 Plans

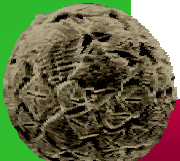
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## **Field**

- Develop a work plan for field-testing.
- Conduct field testing in September.

## **Technology Transfer**

- Input additional documents into the project document database.
- Present at the Sciencetech Stack Emissions Symposium.
- Prepare papers for presentation at the World of Coal Ash and MEGA symposium.



# Contact Information

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