

# The Greenness of Monitoring Methods

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National Water Quality Monitoring Conference

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# ACS Green Chemistry Institute



- ACS Green Chemistry Institute®
  - Founded in 1997 as an independent, nonprofit organization
  - Formed an alliance with the American Chemical Society in 2001
  
- Mission: to advance the implementation of green chemistry principles into all aspects of the chemical enterprise.
  - Research
  - Education
  - Policy Advocacy
  - Industrial Implementation
  - International Cooperation
  - Conferences & Awards

[www.acs.org/greenchemistry](http://www.acs.org/greenchemistry)



# Annual Green Chemistry & Engineering Conference



- 12<sup>th</sup> Annual Green Chemistry & Engineering Conference, June 24-26, 2008
- Advanced registration discount until June 9
- 450-500 attendees for past 3 years
- [www.GCandE.org](http://www.GCandE.org)

CALL FOR PAPERS		Abstracts due February 13, 2008
<p><b>12th Annual Green Chemistry &amp; Engineering Conference</b></p> <p><i>Using Green Chemistry &amp; Engineering to Advance Sustainable Solutions</i></p> <p>CAPITAL HILTON, WASHINGTON, DC June 24–26, 2008</p>		
<p>Join us in June as we continue the journey to sustainability</p>		



# Outline



- Green environmental monitoring introduction
- Developing greenness profiles for the National Environmental Methods Index (NEMI)
- Examples comparing NEMI greenness profiles
  - Measuring organics in water
  - Measuring total residual chlorine in water
  - Measuring lead in water
- General findings regarding NEMI greenness profiles
- How to develop greener methods



# Environmental Monitoring



- New advances in
  - instrumentation
  - quantification
  - characterization of analytes
  - environmental testing
- But in many instances, the analytical methods are not very sustainable or “green”, often using
  - hazardous solvents and reagents
  - generating large quantities of waste
  - using large amounts of energy



# Green Environmental Monitoring Methods



- Green analytical chemistry includes:
  - using fewer hazardous solvents
  - using safer chemicals
  - preventing waste
  - conserving energy
  
- Many aspects of an analytical method affect the “greenness” of a method, including:
  - sample preparation
  - measurement/detection
  - reagents (chemical reaction, digestion, etc.)
  - solvents (extractions, carrier fluid, etc.)
  - preservatives
  - waste (quantity, toxicity)



# “Greener” Analytical Methods in NEMI



- Goals:
  - To provide “greenness” profiles for the analytical methods in the National Environmental Methods Index,
  - and the data so NEMI users can make more informed decisions when selecting a method.
  - The method selected must also meet the desired performance criteria.
- Outcome: Evaluated over 800 analytical methods in NEMI and integrated the greenness profiles.
- Now available at [www.nemi.gov](http://www.nemi.gov).



# NEMI Homepage

## www.nemi.gov



- Searchable, free, online database
- Contains 1000+ methods
- Dynamic
- Useful for searching, comparing & downloading methods
- 6500 visitors per month



**National Environmental Methods Index**

**NEMI v2.0**

- Launch NEMI
- Disclaimer
- What is NEMI?
- Background
- Present & Future
- What's New?
- Method Submission
- Other Information
- Links of Interest
- Help/FAQ

**help NEMI grow**

Click here to partner with the USGS and the EPA

Please send us your **FEEDBACK**

**NEMI is a free, searchable clearinghouse of methods and procedures for both regulatory and non-regulatory monitoring purposes for water, sediment, air and tissues.**

Use **NEMI** first to compare and contrast the performance and relative cost of analytical, text, and sampling methods for environmental monitoring.

### SEARCH NEMI

**Quick/Advanced Search**  
Use this option for a quick search for methods by **analyte name** or **code** (CAS\* number)

**General Search**  
Select a specific method by method number or search for methods under general categories

**Regulatory Search**  
Search for methods approved for **drinking water** or **wastewater regulations**

**Browse All Methods** - List of all methods in NEMI

**NEW! "Greener" Methods Profiles**

Working with the Methods Board and the NEMI Steering Committee, the American Chemical Society's Green Chemistry Institute has completed the initial work and the results as applied to the methods in NEMI can be viewed at [this beta-test query interface](#).

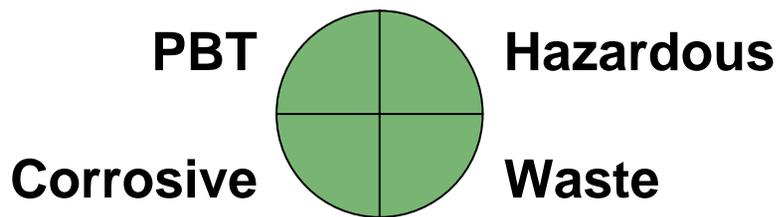
[read more about the greener methods project here...](#)

**Beta: Population/community Biological Protocols**

**Beta: Toxicity Tests**



# Selection Criteria and Symbol



Green-filled quadrant = the method passes the selection criteria defined for that quadrant.

## □ Selection Criteria

- Translate info. from methods into “greenness” profile
- Specifically defined criteria
- Developed in collaboration with 25+ methods experts from 5 Federal agencies, State, and private labs
- U.S. Environmental Protection Agency, U.S. Geological Survey, FDA, NOAA, DOE, private labs



# Selection Criteria



A method is “less green” if:

- ❑ PBT – A chemical used in the method is listed as persistent, bioaccumulative, and toxic (PBT), as defined by the EPA’s Toxic Release Inventory (TRI)<sup>1</sup>.
- ❑ Hazardous – A chemical used in the method is listed on the TRI<sup>1</sup> or on one of the RCRA’s D, F, P or U hazardous waste lists<sup>2</sup>.
- ❑ Corrosive – pH during the analysis is  $< 2$  or  $> 12$ .
- ❑ Waste – Waste amount generated is  $> 50$  g.

<sup>1</sup>Emergency Planning and Community Right-to-Know Act; Section 313; Toxic Release Inventory (TRI), reporting year 2004, (available on the internet at <http://www.epa.gov/tri/chemical/>).

<sup>2</sup>Code of Federal Regulations, Title 40, Part 261, (available on the internet at <http://ecfr.gpoaccess.gov>).



# Two Search Modes in NEMI



- Choice of two search modes in NEMI, both with greenness profiles included:
  - Analyte Search – search for all methods in NEMI for a particular analyte
  - General Search – search for all methods in NEMI for a particular **media type** (water, soil, etc), **method type** (organic, inorganic, radiochemical, microbiological, etc) or **instrument**



# Analyte Search screen with greenness profiles



This is the beta version of an Analyte Query that includes a "Greenness" Rating by the Green Chemistry Institute.

This page is currently under construction, so features may be added or removed before it goes to production. Feel free to test and submit **comments** on its functionality. If something appears "broken", wait several hours or a day and try again--there is active development going on on this page.

### Select Search Criteria

**Analyte Name or Code (required)**

Analyte Name:

- OR -

Analyte Code:

---

Media Name\* :

Method Source\* :

Instrumentation\* :

Method Subcategory\* :

\* optional

[View Results in a New Window \(Printable Format\)](#)  
[Export results for Microsoft Excel](#)  
[Export results as a tab separated text file \(can be opened in any text editor or spreadsheet\)](#)

Analyte: [Aldrin \(309-00-2\)](#) [Click for list of synonyms](#)

6 methods were found in NEMI that match your criteria for the analyte aldrin.

#### Criteria Summary:

- Media Name equals WATER ORA-01403: no data found

Method Number (Sort)	Source (Sort)	Method Descriptive Name (Sort)	Detection Level	Detection Level Type	Bias	Precision	Spiking Level	Instrumentation	Relative Cost (Sort)	Greenness Profile
505	EPA-NERL	Pesticides and PCBs in Water GC-ECD	.007 ug/L	MDL	106 % Rec. (SL)	20 RSD. (SL)	.05 ug/L	GC-ECD	\$\$\$	+
508	EPA-TSC/NERL	Chlorinated Pesticides in Water Using GCECD	.014 ug/L	MDL	66 % Rec. (SL)	9 RSD. (SL)	.075 ug/L	GC-ECD	\$\$\$	+
508.1	EPA-OGWDW/TSC	Chlorinated Pesticides, Herbicides, and Organohalides in Water by GCECD	.009 ug/L	MDL	80 % Rec. (SL)	37.5 RSD. (SL)	.01 ug/L	GC-ECD	\$\$\$	+
525.2	EPA-NERL	Organics in Water Using GCMS	.11 ug/L	MDL	80 % Rec. (SL)	9.3 RSD. (SL)	.5 ug/L	GC-MS	\$\$\$	+
608	EPA-EAD	Organochlorine Pesticides and PCBs via GC with Electron Capture Detector (ECD)	.004 ug/L	MIDL	85 % Rec. (ML)	19 RSD. (ML)	1 ug/L	GC-ECD	\$\$\$	+
625	EPA-NERL	Base/Neutral and Acid Organics in Wastewater	1.9 ug/L	MDL	95 % Rec. (ML)	55 RSD. (ML)	10 ug/L	GC-MS	\$\$\$	+



# Closer View search results



Analyte: Aldrin (309-00-2) [Click for list of synonyms](#)

6 methods were found in NEMI that match your criteria for the analyte aldrin.

#### Criteria Summary:

- Media Name equals WATER ORA-01403: no data found

## Greenness Profiles



Method Number (Sort)	Source (Sort)	Method Descriptive Name (Sort)	Detection Level	Detection Level Type	Bias	Precision	Spiking Level	Instrumentation (Sort)	Relative Cost (Sort)	Greenness Profile
505	EPA-NERL	Pesticides and PCBs in Water GC-ECD	.007 ug/L	MDL	106 % Rec. (SL)	20 RSD (SL)	.05 ug/L	GC-ECD	\$\$\$	
508	EPA-TSC/NERL	Chlorinated Pesticides in Water Using GCECD	.014 ug/L	MDL	66 % Rec. (SL)	9 RSD (SL)	.075 ug/L	GC-ECD	\$\$\$	
508.1	EPA-OGWDW/TSC	Chlorinated Pesticides, Herbicides, and Organohalides in Water by GCECD	.009 ug/L	MDL	80 % Rec. (SL)	37.5 RSD (SL)	.01 ug/L	GC-ECD	\$\$\$	
525.2	EPA-NERL	Organics in Water Using GCMS	.11 ug/L	MDL	80 % Rec. (SL)	9.3 RSD (SL)	.5 ug/L	GC-MS	\$\$\$	
608	EPA-EAD	Organochlorine Pesticides and PCBs via GC with Electron Capture Detector (ECD)	.004 ug/L	MIDL	85 % Rec. (ML)	19 RSD (ML)	1 ug/L	GC-ECD	\$\$\$	
625	EPA-NERL	Base/Neutral and Acid Organics in Wastewater	1.9 ug/L	MDL	95 % Rec. (ML)	55 RSD (ML)	10 ug/L	GC-MS	\$\$\$	

[www.nemi.gov](http://www.nemi.gov)

Maintained by [disulliv@usqs.gov](mailto:disulliv@usqs.gov)

Click on a greenness profile for more information (see next slide)



Greenness  
profile  
information  
pop-up  
window  
provides the  
data behind  
the profile

## Greenness Profile Summary

Method Number	525.2
Analytical Sample Amt (mL)	1000
Analytical Sample Amt (g)	1000
pH of Analytical Sample	<2
Calculated Waste Amt (g)	1,053.8
PBT	Green
Toxic	Not Green
Corrosive	Not Green
Waste	Not Green
Assumptions/Comments	Cartridge extraction procedure is used as the consumption of chemicals is larger in comparison with disk extraction procedure.

N.S. -- not specified  
N.A. -- not applicable

## Chemicals in Method

Chemical Name	Concentration	Solution Amt (mL)	Density	Chemical Amt (g)
METHYLENE CHLORIDE	-	12	1.33	15.9
ETHYL ACETATE	-	10	.9	9.02
METHANOL	-	15	.79	11.85
WATER	-	10	1	10
ANHYDROUS SODIUM SULFATE	-	-	-	7



# Examples – comparing NEMI greenness profiles

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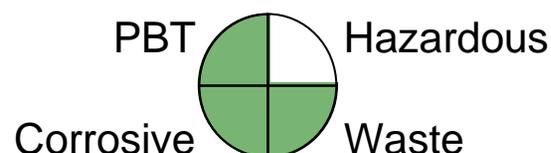
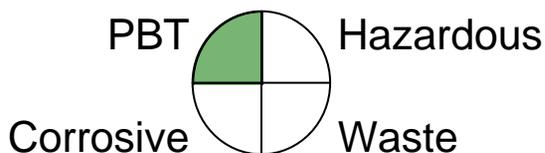
- Measuring organics in water
- Measuring total residual chlorine in water
- Measuring lead in water



# Measuring Organics in Water



Two EPA methods for determining organic pesticide residues in water, such as aldrin, using gas chromatography:



## EPA Method 525.2

- Extraction of 1L sample
- **PBT – none**
- Hazardous – ethyl acetate, methylene chloride, methanol
- Corrosive – pH < 2
- Waste – > 50g waste

## EPA Method 505

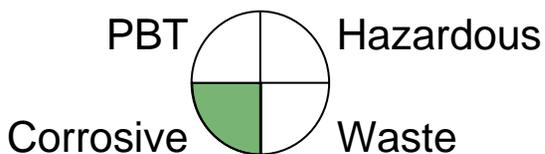
- Extraction of 35g sample with 2g hexane
- **PBT – none**
- Hazardous – hexane
- **Corrosive – no acid/base**
- **Waste – < 50g waste**



# Measuring Total Residual Chlorine in Water

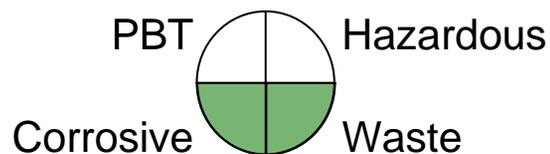


Three EPA methods for measuring Total Residual Chlorine in natural and treated water:



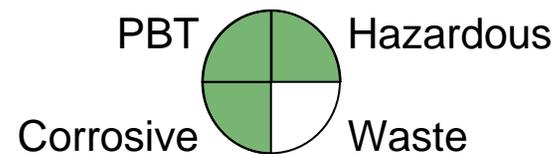
## EPA Method 330.4

- Titration of 100 ml sample
- PBT – mercuric chloride preservative
- Hazardous –  $\text{HgCl}_2$
- Corrosive –  $\text{pH} < 4$
- Waste –  $> 50\text{g}$  waste



## EPA Method 330.5

- Spectrophotometric method with 10 ml sample
- PBT – mercuric chloride preservative
- Hazardous –  $\text{HgCl}_2$
- Corrosive –  $\text{pH} < 4$
- Waste –  $< 50\text{g}$  waste



## EPA Method 330.3

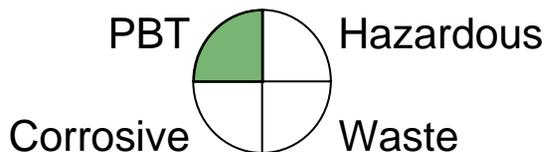
- Titration of 200 ml sample
- PBT – none
- Hazardous – none
- Corrosive –  $\text{pH} < 4$
- Waste –  $> 50\text{g}$  waste



# Measuring Lead in Water

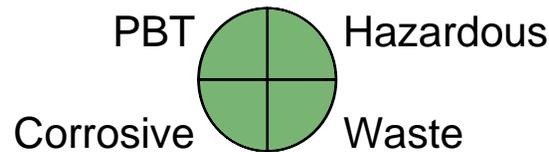


Two methods for measuring lead in water:



## Standard Methods 3500-Pb-B

- Lead dithizonate is formed and measured with a spectrophotometer
- **PBT – none**
- **Hazardous – chloroform, citrate cyanide solution**
- **Corrosive – pH < 2**
- **Waste – > 50g waste**



## USGS Method I-1401-85

- Injection of 20  $\mu\text{L}$  of water sample with 5  $\mu\text{L}$  matrix modifier solution into a GFAA spectrometer
- **PBT – none**
- **Hazardous – none**
- **Corrosive – no**
- **Waste – < 50g waste**



# General Findings Regarding NEMI Greenness Profiles



ACS  
Green  
Chemistry  
Institute

- 2/3 of methods failed waste criterion
  - Organic analyses mostly fail due to extractions with solvents
  - Inorganic analyses mostly fail due to mineral acids for preservation or digestion
    - Creative, greener examples use small sample sizes and generate < 50g waste
- 1/2 of methods failed hazardous chemical criterion
  - Greener examples use safer chemicals or eliminate chemicals
- 1/5 of methods failed the pH criterion
  - Greener examples use neutral pH, buffers, or refrigeration (in the case of preservation)
- 1/20 of methods failed the PBT criterion
  - Mostly by using lead (digestion), mercury (preservation)

Reference: Keith, L. H.; Gron, L. U.; Young, J. L. "Green Analytical Methodologies" *Chemical Reviews*, **2007**, 107, 2695-2708.



# How to Develop Greener Methods



- Develop methods with:
  - fewer hazardous solvents
  - safer chemicals
  - less waste
  - less energy
- Use greenness profile selection criteria as guidance to find alternative strategies
- Learn from the greener methods in NEMI

Reference: Keith, L. H.; Gron, L. U.; Young, J. L. "Green Analytical Methodologies" *Chemical Reviews*, **2007**, 107, 2695-2708.



## Poster #18

*Defining the Greenness of  
Monitoring Methods*

Today, 2:30-3:30 pm



# Acknowledgements

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- Dr. Paul Anastas
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Thank You!

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