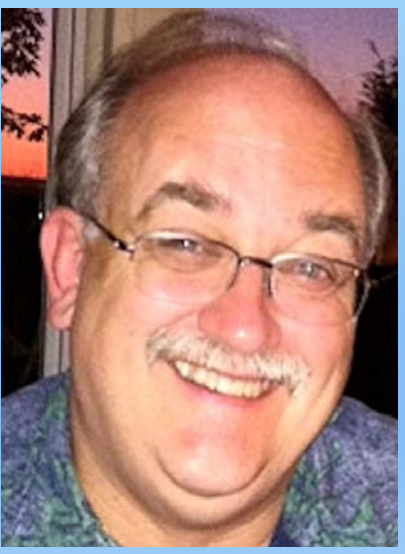
# They Said It Couldn't Be Done: A Brief History of Environmental Water Monitoring



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# Disclaimer

- The information in this presentation has *not* been reviewed by the USEPA
- The views and opinions are those of the presenter
- He's old, fat, balding, and cranky, so watch out
- Despite that, he's been supporting various USEPA projects for over 30 years

# In the beginning …

- There was water, and it got dirty
- And that was *not* good
- The U.S. Geological Survey, formed in 1876, was responsible for early water monitoring efforts
- The American Public Health Association published the first edition of *Standard Methods for the Examination of Water and Wastewaters* in 1906
- The ASTM D-19 Committee on water monitoring was created in 1932
- The National Sanitation Foundation was established in 1944

# Pollution in Popular Culture

In 1965, mathematician and satirist Tom Lehrer composed his song "Pollution" that included the lyrics:

*If you visit American city,*
*You will find it very pretty.*
*Just two things of which you must beware:*
*Don't drink the water and don't breathe the air.*

*Pollution, pollution,*
*They got smog and sewage and mud.*
*Turn on your tap and get hot and cold running crud.*

# Pollution in the News

- On June 20, 1969, the Cuyahoga River in Cleveland, Ohio caught fire (again)
- It was at least the thirteenth major fire on the river in 100 years
- It made national news
- Public outrage over the fire prompted political action that spurred the creation of the U.S. Environmental Protection Agency

# U.S. Environmental Protection Agency

- Formed in 1970
- The Clean Water Act was enacted in 1972
- The Safe Drinking Water Act was enacted in 1974
- Problem solved, right?

Not quite …

# Parameters that were monitored

- Most of the parameters were driven by “sanitary” chemistry and included:
  - BOD
  - COD – by permanganate
  - Total suspended solids
  - Total solids
  - pH
  - Coliform bacteria by multiple tube fermentation

# Monitoring Technologies

- In the early 1970s, most monitoring of water quality was still done via simple colorimetric methods
- Industrial effluents were monitored for a few contaminants at milligram per liter levels, what we now call “chunks”
- By law, EPA was responsible for approving State monitoring programs, but not much else

# Monitoring Requirements

- EPA established facility-specific permit requirements for monitoring in:
  - Wastewater
  - Pre-treatment of discharges to sewer systems
  - Sewage sludge (wastewater treatment residuals)
- Drinking water monitoring requirements were implemented at a national-level and with a laboratory certification program

# So how did we move forward?

- Lawyers got involved
- In 1975, the Natural Resources Defense Council (NRDC) filed suit against Russell Train, the EPA Administrator, to force EPA to implement portions of the Clean Water Act
- In 1976, EPA and the plaintiffs entered into a settlement agree via a consent decree
- EPA established the "Priority Pollutant List." To get on the list, a pollutant had to have:
  - Been found in someone's effluent
  - A method
  - Authentic standards available

# Monitoring Methods

- Given the large number of organic pollutants and the court-mandated schedule, EPA decided to use GC/MS as the basic monitoring technology whenever practical
- EPA's laboratories in Cincinnati, OH and Athens, GA developed methods for organics and metals, including:
  - 624 for volatiles
  - 625 for extractable organics
  - 608 for organochlorine pesticides and PCBs as Aroclors
  - 613 for 2,3,7,8- tetrachloro-*p*-dioxin
  - 200-Series flame atomic absorption methods for metals

# 304(h) Proposal in 1979

- EPA proposed a series of methods for monitoring compliance with wastewater discharge permit limits in 1979, under the authority of Section 304(h) of the Clean Water Act
- Public comments flowed in, and in, and in …
- Virtually every aspect of every method was the subject of comment from someone
- Environmental groups generally commented that EPA was being too lax and industry suggested that EPA was going way out on a limb with regard to environmental monitoring
- The use of GC/MS was criticized in general
- Claims were made that GC/MS was not, and never could be, a quantitative technique
- "*It'll never work*" was a common refrain

# Post-proposal Efforts

- Following the 1979 proposal, EPA spent the next five years:
  - Responding to public comments
  - Refining the proposed methods
  - Developing new and improved methods or techniques to support monitoring needs
  - Incorporating newer instrumentation and other developments from instrument manufacturers into the program
- Final promulgation was on October 26, 1984

# New Techniques

- In response to comments about the non-quantitative nature of GC/MS, EPA's Office of Water developed versions of the GC/MS methods that employed isotope dilution as the means of quantifying the pollutants of interest (e. g., 1624 and 1625)
- Isotope dilution was not a new concept. It had been developed in the late 1930s and refined by researchers in various fields over the years.
- It did require that standards of isotopically pure materials be available, so EPA contracted with vendors to prepare the needed isotopically pure standards
- The recovery correction yields improvements in both accuracy and precision (2 to 4 times better)

# Automated Data Processing -1980s

- EPA helped develop systems for automated processing of gas chromatography/mass spectrometry (GC/MS) raw data
  - Worked with Finnigan to develop spectral identification software in the INCOS data system, using System J, a proprietary operating system
  - Developed capability to receive GC/MS raw data on 9-track tape and generate sample-specific analytical results for isotope dilution methods

# Metals Method Improvements

- Analyses of metals were confounded by the multiple forms of many of the metals of concern
- EPA developed sample digestion techniques for “total recoverable metals” in order to capture as many forms of the priority pollutant metals as practical
- Inductively-coupled plasma atomic emission spectrometry (ICP) instruments became available
- EPA developed an ICP method for compliance monitoring

# Methods as of 1984

- As of the 1984 promulgation of Clean Water Act compliance monitoring methods, it was practical to monitor metals and organics at levels of micrograms per liter (µg/L)
- QC techniques had been standardized across most methods
- Appropriate instrument performance checks were developed and included in methods
- QC acceptance criteria were included in methods
- And life was good …

# And then …

- In the late 1980s, some fool researcher discovered dioxins and furans were formed during the manufacturer of paper products via chlorine bleaching of pulp
- The pulp and paper industry was one of the 21 industrial categories in the 1976 consent decree
- The Office of Water (and other EPA Program Offices) responded by developing new methods for dioxins and furans and using those methods to investigate discharges from the pulp and paper industry

# High Resolution GC/MS Methods

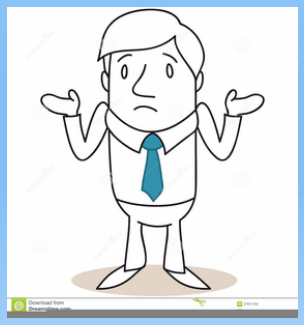
- Method 1613 - for 17 2,3,7,8-substituted dioxins and furans
- Method 1668 – for 209 polychlorinated biphenyl (PCB) congeners
- Method 1614 – for 209 polybrominated diphenyl ether (PBDE) congeners
- All employ mass resolution of ≥ 10,000 to distinguish analyte masses in the 5th decimal place
- All employ isotope dilution

# Low-Level Metals Methods

- Not to be out done, metals researchers realized that some trace metals were present at much lower levels than previously thought
- USGS determined that much of their long-term monitoring data actually represented contamination of the samples during either collection or analysis, or both
- Techniques were available in the oceanographic community to overcome contamination concerns

# “Clean” Metals Techniques

- In the mid-1990s, the Office of Water began developing sampling and analysis methods to overcome these contamination concerns
- A suite of “clean” techniques were drafted, tested, and released by EPA (Methods 1630 to 1640)
- But the skeptics remained unconvinced that they would be effective



# Clean Hands – Dirty Hands

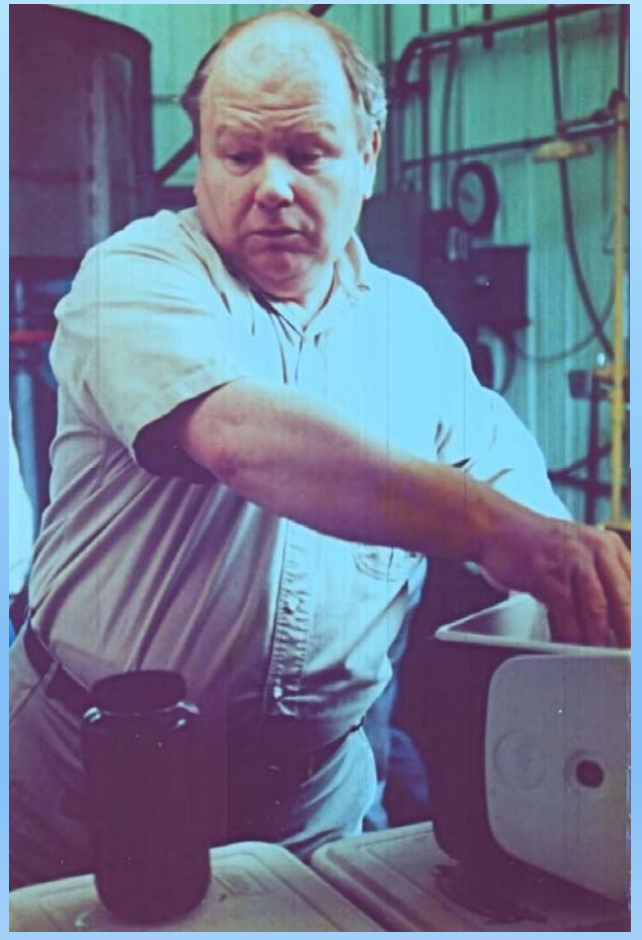
- Method 1669 is the sampling procedure that incorporates "clean hands – dirty hands" sample collection procedures that allow measurement of metals at sub-part-per trillion levels
- EPA developed training on the techniques, including a widely distributed video

# The Cutting Edge of Science

- One of the "conventional pollutants" mentioned by name in the Clean Water Act is "oil and grease"
- Originally used as a process control parameter at wastewater treatment plants
- Methods promulgated in 1984 employed CFC-113 as the extraction solvent
- The "Montreal Protocol" required the elimination of all non-essential uses of CFCs in order to protect stratospheric ozone

# Method 1664

- The Office of Water began studying replacement solvents in 1992
- Extensive testing of different solvents in effluents from a wide range of industrial categories



# Method 1664

- Ultimately, hexane was selected as the replacement solvent of choice
- Method 1664 was proposed in January 1996 and ultimately promulgated in May 1999
- Extensive guidance issued in conjunction with the solvent change, because permittees were not convinced it would work and that the solvent change would cause them to violate their permit limits

# Microbiology Methods

- It's not all chemistry!
- EPA approved wastewater and ambient water methods for:
  - *E. coli*
  - Fecal streptococci
  - Enterococci
- EPA approved ambient water methods for:
  - *Cryptosporidium*
  - *Giardia*
- EPA also approved a method for *Salmonella* in biosolids
- Techniques include multiple-tube fermentation and membrane-filtration
- Although not yet approved at 40 CFR Part 136, EPA has validated four qPCR methods for ambient waters: two for enterococci (1609, 1611) and two for microbial source tracking (1696, 1697)

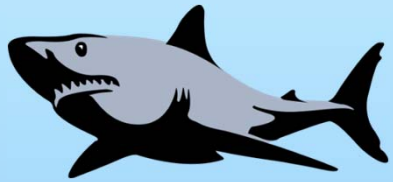
# Whole Effluent Toxicity

- While chemical-specific monitoring methods are important, EPA recognized that there were toxic effects of effluents that could not be traced to specific contaminants
- Embarked on development of procedures for measuring toxicity of "whole effluents" on specific organisms
- Exposure may result in lethal or sublethal effects on organisms
- EPA promulgated methods for measuring whole effluent toxicity (WET) in 1995
- Industry sued EPA over implementation of WET methods, claiming that they were not adequate or accurate enough for required use

# WET Round Robin Study

- In response to the law suit, EPA worked with industry to design and implement a large-scale multi-laboratory round robin study of WET methods
- Largest study of WET procedures ever conducted
  - 12 of the 17 approved WET test methods evaluated
  - 56 different laboratories involved, each testing an average of 3 methods
- Industry still baulked at the use of the methods
- EPA repeatedly defended the methods and study results through the courts, ultimately prevailing in December 2004, but permit-specific challenges continue to today

# Just when you thought it was safe to go back in the water …



- Researchers showed that pharmaceuticals, personal-care products, hormones, and steroids can be present in drinking water drawn from surface waters influenced by wastewater discharges
- These pollutants are not all amenable to GC/MS, so EPA has developed LC/MS/MS procedures, many of which use isotope dilution, and monitor parent/daughter ion pairs
- And maybe you have heard of per- and polyfluoroalkyl substances (PFAS)?

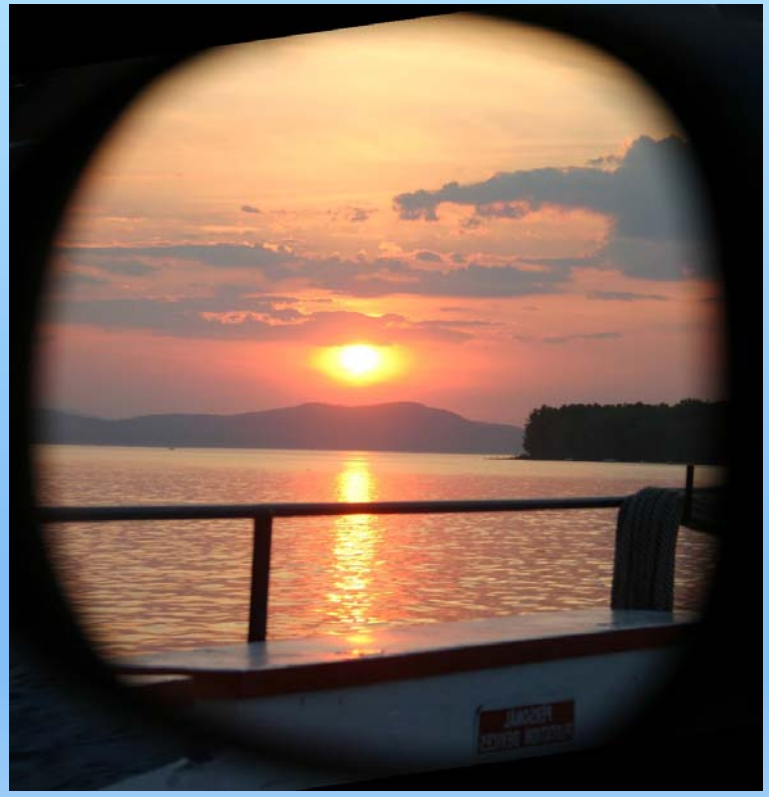
# Where to next?

- PFAS in various matrices – *"it's everywhere, it's everywhere!"*
- Continuous on-line monitoring – *how can we use large amounts of data to assess compliance against existing limits?*
- qPCR for microbial pollutants in wastewater – *again, skeptics abound*

# Something to Keep in Mind

As we move forward, it pays to keep an eye on what is behind us.

We never know what we might learn.




Questions?