History of the Clean Water Act: Everything you wanted to know about EPA, but were afraid to ask

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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 Nation Sanitation Foundation was established in Michigan in 1944.

U. S. Environmental Protection Agency

- Formed in 1970
- The Clean Water Act was enacted in 1972
  - President Nixon had vetoed the bill on October 17th and the House and Senate promptly overrode his veto on the 18th.
  - The Act created a major Federal initiative.
  - In the 1970's only 80 million people (40% of a total US population of 200 million) had secondary treatment of their wastewater.

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 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”
- The Cuyahoga River drew national attention when it caught fire in the summer of 1969
- By law, EPA was responsible for approving State monitoring programs, but not much else

Monitoring Method Requirements

- EPA established requirements for monitoring in:
  - Wastewater under the Clean Water Act (approved methods listed at 40 CFR Part 136 (permit)
  - Pre-treatment of discharges to sewer systems (approved methods listed at 40 CFR Part 136 (permit)
  - Sewage sludge (wastewater treatment residuals) (approved methods listed at 40 CFR Part 136 (permit)
  - Drinking Water under the Safe Drinking Water Act (approved methods listed at 40 CFR Part 141, and implemented at a national-level laboratory certification program)

Water Quality Standards

- Ambient water quality monitoring and surveys
- Methods from various sources may be used, provided that they meet the study objectives
- Some microbiological methods for ambient water monitoring are listed at 40 CFR Part 136
- Surveys of Great Lakes water quality involved methods developed by academic contractors or grantees hired by EPA and the States

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 implement the portions of the Clean Water Water that dealt with Section 307(a), for the "toxic" pollutants. (NRDC *et al. v.* Train. 8 ERC 2120)
- In 1976, EPA and the plaintiffs entered into a settlement agree via a consent decree

Toxic Pollutant List, No, the Priority Pollutant List

Derivation - Starting with the list of toxic pollutants, EPA used five criteria to select the priority pollutants:

1. We included all pollutants specifically named in the original Consent Decree
2. There had to be a chemical standard available for the pollutant, so that testing for the pollutant could be performed
3. The pollutant had to be reported as found in water with a frequency of occurrence of at least 5% (based on the Schackleford & Keith Report, "*Organics Identified in Water*," USEPA);

Toxic Pollutant List, No, the Priority Pollutant List (continued)

4. The pollutant had to be produced in significant quantities, as reported in Stanford's Research Institutes' "1976 Directory of Chemical Producers, USA," and
5. The thirteen metals in the Consent Decree had the term, "and their compounds." This was interpreted to mean "total metals," that would include both inorganic and organic metals.

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, 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
  - ICP method for metals

304(h) Proposal

- 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

Industry Response

- Not surprisingly, the comments from 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.
- In response, EPA began a long-running series of meetings on analysis of pollutants in the environment, aka, the Norfolk meeting, that ran for 26 years.

Promulgation of Methods - 1984

- 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.
- 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.

Isotope Dilution

- The Office of Water contracted with vendors to prepare the needed isotopically pure standards
- The Office of Water developed Methods 1624 and 1625
  - Based on Methods 624 and 625
  - Added isotope dilution to reduce the variability in analyte results
  - Isotope dilution corrects analyte results for the recovery of the labeled compound added to the sample before any other processing
  - Overall improvements in both precision and accuracy

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.
  - Practically speaking, "total recoverable metals" = "total metals"
- Inductively-coupled plasma atomic absorption 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 (ug/L)
- Quality control techniques had been standardized across methods
- Appropriate instrument performance checks were included in methods
- QC acceptance criteria were included in methods

Asbestos

- Developed method for analysis of asbestos in wastewater samples at EPA Athens R&D laboratory
- Transmission electron microscopy

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

- In order to measure dioxins and furans at very low (part per quadrillion) levels and accurately identify the analytes in the presence of various interferences, the Office of Water relied on gas chromatography and high resolution mass spectrometry (HRMS)
- Mass resolution of 10,000 allows the instrument to distinguish among analytes whose exact masses differ in the fifth decimal place
- Isotope dilution used as well
- Conducted a round-robin validation study involving 21 labs in 5 countries.

High Resolution GC/MS Methods

- EPA Method 1613 - for 17 2,3,7,8-substittued dioxins and furans (1990)
- EPA Method 1668 – for 209 polychlorinated biphenyl (PCB) congeners (1997)
- EPA Method 1614 – for 209 polybrominated diphenyl ether (PBDE) congeners (flame retardants) (2003)

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 (predominantly for dissolved metals)
- 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
- 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

1600-Series Metals Methods

- **Method 1630:** Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry
- **Method 1631:** Mercury in Water by Oxidation, Purge and Trap, and CVAFS
- **Method 1631 Appendix A:** Digestion Procedures for the Determination of Total Mercury in Tissues, Sludge, Sediments, and Soils
- **Method 1632:** Inorganic Arsenic in Water by Hydride Generation Quartz Furnace Atomic Absorption Spectrometry
- **Method 1632A:** Chemical Speciation of Arsenic in Water and Tissue by Hydride Generation Quartz Furnace Atomic Absorption Spectrometry

1600-Series Metals Methods (cont.)

- **Method 1637:** Determination of Trace Elements in Ambient Waters by Chelation Preconcentration with Graphite Furnace Atomic Absorption Spectrometry
- **Method 1638:** Determination of Trace Elements in Ambient Waters by Inductively Coupled Plasma-Mass Spectrometry
- **Method 1639:** Determination of Trace Elements in Ambient Waters by Stabilized Temperature Graphite Furnace Atomic Absorption Spectrometry
- **Method 1640:** Determination of Trace Elements in Ambient Waters by On-Line Chelation Preconcentration and Inductively Coupled Plasma-Mass Spectrometry

Other Metals Method Materials

- Guidance on Establishing Trace Metals Clean Rooms in Existing Facilities
- Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring
- **Method 1669:** Sampling Ambient Water for Determination of Metals at EPA Water Quality Criteria Levels
- Video: Sampling Ambient and Effluent Waters for Trace Metals

Method 1631

- Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry
- Developed to determine mercury reliably at ambient water quality criteria (WQC) levels

		Lowest WQC
Method Range:	0.5 - 100 ng/L	Human health = 1.8 ng/L
MDL:	0.2 ng/L	Wildlife = 1.3 ng/L

Method 1669

- Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels
  - Incorporates clean techniques from USGS and other experts
  - Provides procedures necessary to produce reliable results at the lowest water quality criteria published by EPA
  - Designed to support collection of ambient water samples
  - Performance-based

The Cutting Edge of Science

- “Oil and grease” – A Clean Water Act “conventional pollutant”
- 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
- No solvent mimicked CFC-113 exactly
- Ultimately, hexane was selected as the replacement solvent of choice, because it had been used as the solvent before the use of CFC-113, and was a choice of convenience
- Method 1664 was proposed in January 1996 and ultimately promulgated in May 1999.
- Extensive guidance issued in conjunction with the solvent change

Cyanide

- Cyanide occurs in wastewater samples in multiple forms
- Some forms are defined by the measurement or treatment technique (e.g., cyanide amenable to destruction by chlorination)
- Currently approved methods for:
  - Total cyanide
  - Available cyanide
  - Free cyanide
- Wide variety of instrumentation applicable to these measurements

Microbiology Methods

- It's not all chemistry
- EPA has approved wastewater methods for 8 microbiological parameters:
  - 4 forms of coliform bacteria (2 fecal and 2 total)
  - *E. coli*
  - Fecal streptococci
  - Enterococci
  - *Salmonella*
- EPA also approved methods for monitoring ambient water for:
  - *Cryptosporidium*
  - *Giardia*

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

Whole Effluent Toxicity

- EPA promulgated methods for measuring whole effluent toxicity (WET) in 1995
- Use of WET methods was not universally needed, but adopted on a case-by-case basis in discharge permits for specific facilities.
- Industry sued EPA over the implementation of WET methods, claiming that they were not adequate or accurate enough for required use

WET Round Robin Study

- In response to 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:
  - Fifty-five labs participated in this study
  - 7 to 29 labs per method.
- Industry still baulked at the use of the methods and even on the completion of the study, litigation continued for two years.
- EPA repeatedly defended the methods and study results through the courts, ultimately prevailing in June 2006

And now?

- EPA faces new challenges, including:
  - the management of pharmaceuticals, personal care products and PFOA/PFOS;
  - those presented by designer pesticides
  - and the control nutrients and sediment in ecosystems and watersheds.
- EPA is also dealing with managing eutrophication of water bodies, issues with whole ecosystems, the Chesapeake Bay, the Great Lakes and the Gulf of Mexico.

Where to next?

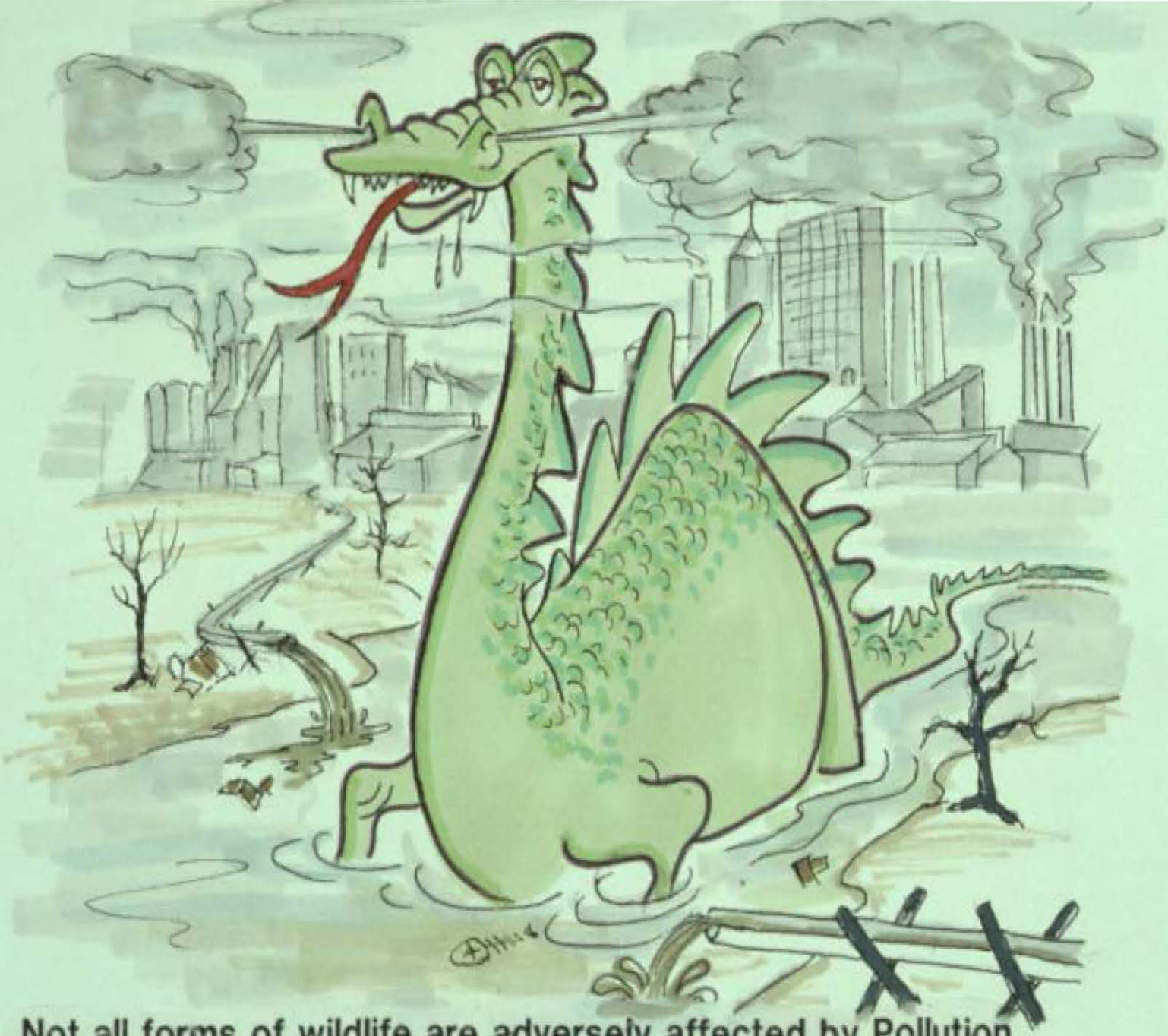
- On-line monitoring
  - Continuous analysis
  - Can be applied to both effluents and ambient water monitoring
- Total nitrogen – replace current measurements for 4 or more components

Demonstration Projects

- On-line continuous monitoring will be demonstrated in projects conducted in:
  - Puget Sound
  - Chesapeake Bay
- Focus on nutrients responsible for eutrophication
- ASTM's D -19 Committee is developing a guidance document on on-line monitoring with:
  - Performance specifications
  - Quality assurance

On-Line monitoring

- EPA is supporting the ASTM efforts
- ISO has released Method 539, which is a general guidance document for on-line monitoring.
- Plan to use the guidance as a outline for more robust on-line monitoring methods and programs.



Not all forms of wildlife are adversely affected by Pollution

Questions?