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science for a changing world

Emerging Contaminants
A Water-Quality Odyssey

NCWRA Forum
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U.S. Geological Survey

Major Topics

- Background information
- Recent investigations
- Ongoing research
- Implications for the future

What are “emerging contaminants?”

Christian Daughton, PhD, USEPA

“…previously unknown, unrecognized, unanticipated, or unsuspected chemical pollutants”

Daughton and Ternes, 1999, Pharmaceuticals and personal care products in the environment: Agents of subtle change?

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Some emerging contaminants through the ages

- Silt and salt
- Pathogens
- Metals and fossil fuels
- Priority pollutants

"We learn from history that we do not learn from history."

--Georg W. Hegel (1770-1831)

Silt and salt

Gilgamesh, 2700 B.C.

- Deforestation
- Erosion, siltation, and flooding
- Salt buildup in soils and ground water
- Decline of coastal cities as deltas migrated
- ✪ Some cultures established “sacred groves” and practiced terracing, crop rotation, tree planting

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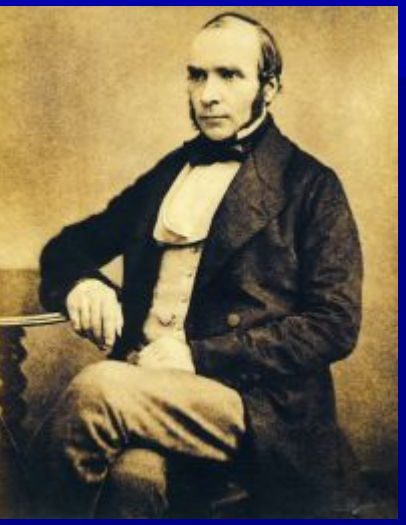
Pathogens



John Snow, M.D.
father of
epidemiology

- Cholera epidemics
  - Cultures with stringent hygiene practices had less disease
  - Rise of modern water and sewer sanitation systems and public health programs
  - Understanding of waterborne illness and germ theory

Metals and fossil fuels

Alice Hamilton, M.D.
founder of occupational medicine

- Metals (e.g., lead)
- Fossil fuels
  - Coal
  - Oil, gas, and fuel additives
    - Tetra-ethyl lead
    - MTBE
- ✪ Occupational health initiatives

Priority pollutants

Rachel Carson
conservationist
and author

- List established in the 1970's
  - Litigation settlement
  - 126 Chemicals of concern that could be measured with available technology
- Toxic, persistent, and bioaccumulative pollutants
  - Heavy metals
  - Polycyclic aromatic hydrocarbons
  - "Dirty dozen" (PCBs, dioxins, DDT, etc.)
- ✪ Water-quality criteria and effluent limitations

Current Headlines

"So-Called 'Intersex Fish' Suggest New Pollution Problem"

"Flame Retardants: Alarming Increases in Humans and the Environment"

"Threat Seen from Antibacterial Soap Chemicals"

Today's emerging contaminants

- Household, industrial, and agricultural chemicals
  - Cleaners and solvents
  - Fire retardants and plasticizers
  - Pesticides and disinfectants
- Pharmaceuticals and personal care products
  - Fragrances
  - Hormones
  - Antibiotics and other drugs

Sources and significance

- Sources
  - Wastewater
  - Other
- Why are they important?
  - Widely used in quantity
  - Continuously released
  - Potentially affect health (e.g., endocrine disruption)

Landmark investigations

- Studies in Europe, late ‘80s – early ‘90s
- USGS national reconnaissance, 1999-2000 (Kolpin et al., 2002)

- 139 streams in 30 states; focused on susceptible sites
- 95 analytes; 82 detected
- Detections in 80% of streams
- Mixtures common

Dana Kolpin, USGS
Research Hydrologist

You only find what you look for

- Analytical methods are developing in parallel with environmental studies
  - Low level (< 1 μg/L)
  - Water, solids, tissue
  - Target analytes & reporting levels evolve
- USGS methods test for many compounds, but still a fraction of the chemicals in existence

Chemist Chris Lindley, USGS National WQ Lab, installs a new GC/MS/MS system

More landmark studies

- Persistence of contaminants in a drinking-water plant, NJ (Stackelberg et al., 2004)
  - Sampled from multiple process streams
  - 106 analytes; 40 detected
  - Fate varied
- Survey of contaminants in biosolids destined for land application (Kinney et al., 2006)
  - 9 biosolid products from municipal WWTPs
  - 87 analytes; 55 detected; 30-45 in each
  - Biosolids are “highly enriched” compared to effluents or receiving waters

Investigations in North Carolina

1. Emerging contaminants (EMCs) in Triangle Area source-water supplies
2. Pharmaceuticals in drinking water, source water and wastewater, Cape Fear and Tar-Pamlico basins
3. Onsite and offsite wastewater systems: effects on residential streams in the Upper Neuse basin

1. Triangle Area water supplies

TAWSMP Partners

Apex
Cary
Chatham County
Durham
Hillsborough
Morrisville
Orange County
OWASA
Triangle J COG
Wake County
USGS

- Triangle Area Water Supply Monitoring Project (local governments and USGS)
- USGS National Water-Quality Assessment Program (site near Smithfield)

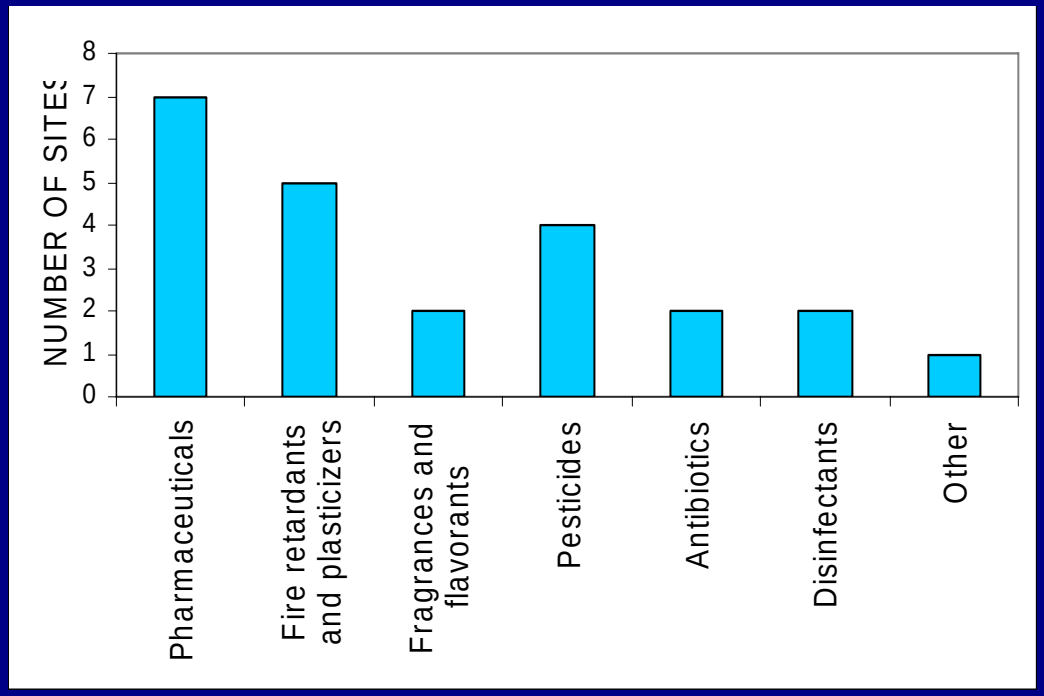
- Objective
  - Occurrence of EMCs in drinking-water supplies in the greater Triangle Area
- Study design
  - Upper Neuse and Upper Cape Fear basins
  - 6 Reservoir and 2 river sites
  - Source water

Protocols and analyses

- No contact with target compounds prior to sampling
- 126 Analytes
  - 63 “Wastewater tracers”
  - 22 Pharmaceuticals
  - 46 Antibiotics

24 Compounds were detected

- 3 Non-prescription pharmaceuticals
- 6 Fire retardants and plasticizers
- 6 Fragrances and flavorants
- 3 Pesticides
- 3 Antibiotics
- 1 Disinfectant
- 2 Other use



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Where and how much?

- At least 1 detected at each location
- Mixtures were common
  - Median = 3.5
  - Maximum = 12
- Concentrations were low
  - Only 1 value > 1 μg/L
  - No exceedances of MCLs, LHAs, or NC water-quality criteria (but few exist)

Triangle results compared with other urban areas

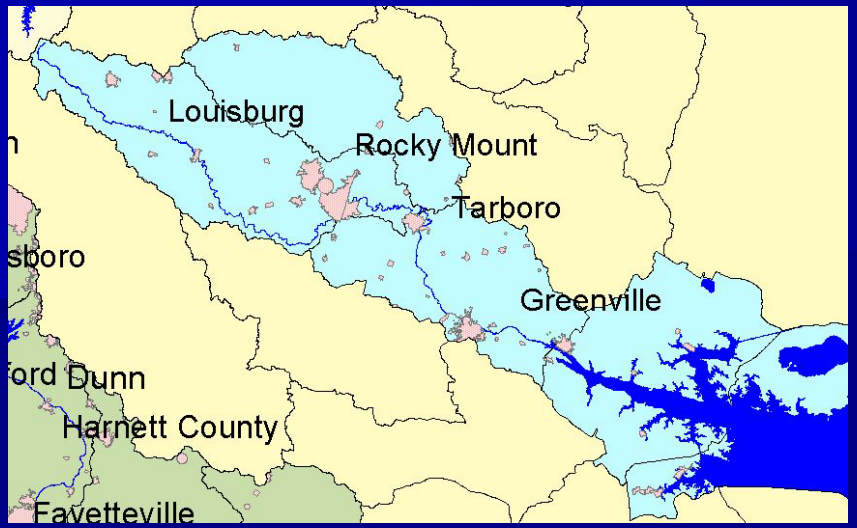
- Similar but fewer compounds were detected
- Concentrations were within ranges observed elsewhere
- Maximum concentrations were generally lower, except for fire retardants
- Differences in study design limit comparisons

2. Occurrence and fate of EMCs in the Cape Fear and Tar-Pamlico basins: From wastewater effluent to finished drinking water

- Centers for Disease Control and Prevention
- Objectives
  - Distribution of pharmaceuticals and wastewater tracers in sources of drinking water
  - Effects of treatment practices on degradation

Approach

- Sampled WWTP effluents and raw drinking-water supplies in each basin
- Selected facilities with different treatment processes to compare fate
- Sampled at multiple stages in selected drinking-water plants to track removal during treatment



- Tar-Pamlico Plants
  - 3 Wastewater
  - 3 Drinking Water

- Cape Fear Plants
  - 7 Wastewater
  - 6 Drinking Water

Compounds most commonly detected in raw drinking-water supplies

	CAPE FEAR	TAR
WASTEWATER COMPOUNDS		
Metolachlor	6/7	2/3
Caffeine	7/7	3/3
Diethoxyoctylphenol	3/7	3/3
Ethoxyoctylphenol	3/7	0/3
Benzophenone	7/7	2/3
Methyl salicylate	6/7	3/3
p-Cresol	3/7	2/3
FYROL CEF	6/7	0/3
FYROL PCF	5/7	0/3
Tributylphosphate	5/7	0/3
PHARMACEUTICALS AND ANTIBIOTICS		
Diphenhydramine	3/7	0/3
Carbamazepine	1/7	0/3

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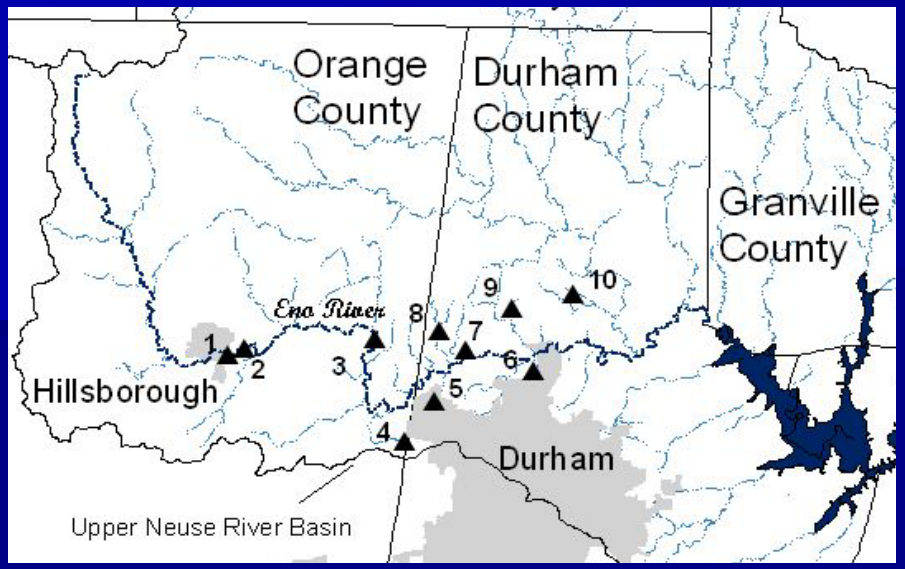
Preliminary findings

- WWTP using UV had more compounds present than those using chlorination
- Low concentrations and few compounds detected in drinking water supplies limit ability to track removal through the treatment process

3. Effects of centralized and onsite wastewater treatment practices

- Collaborators
  - NC Division of Environmental Health
  - North Carolina State University
  - Virginia Polytechnic Institute and State University
- Objective:
  - Are there differences in stream WQ associated with onsite vs. offsite wastewater treatment?



- Upper Neuse study area
  - 2 Eno River sites
  - WWTP effluent
  - 3 “sewered” streams
  - 3 “septic-tank” streams
  - 1 undeveloped stream

- Multiple analytes
  - Conventional
  - Fecal coliforms
  - Wastewater tracers
  - Antibiotics
  - Optical brighteners

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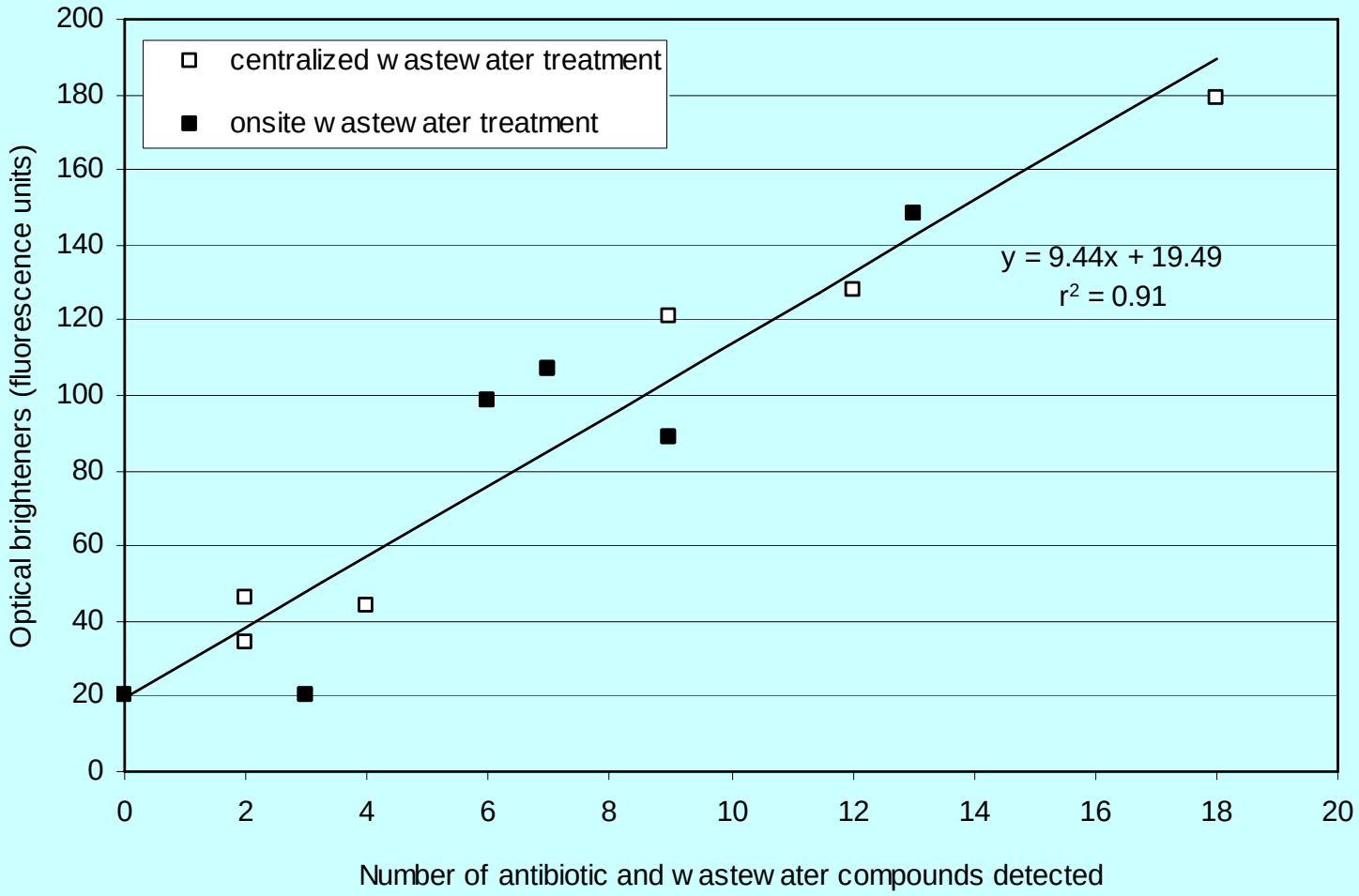
Results for emerging contaminants

- 95 analytes; 44 detected
- Most frequently found
  - Fragrances and flavorants
  - Detergent metabolites
  - Flame retardants and plasticizers
  - Sterols
  - Metolachlor
  - Caffeine and carbamazepine
  - Azithromycin, erythromycin, tylosin

Findings for small streams

- Nitrate was higher where wastewater is treated by onsite (septic) systems
- Similar frequencies of detection for wastewater compounds and antibiotics—low concentrations of both
- Site showing greatest effects of wastewater appeared to have a leaking sewer line
- Detection of EMCs was correlated with optical brighteners (detergent additives)

Relation of optical brightener fluorescence to number of antibiotic and wastewater compounds for samples from small streams



Follow-up study in progress

- Evaluate utility of optical brighteners as a screening tool for wastewater in small drainage basins
- Potential application for locating sewer line breaks and failing septic systems

What we know about EMCs

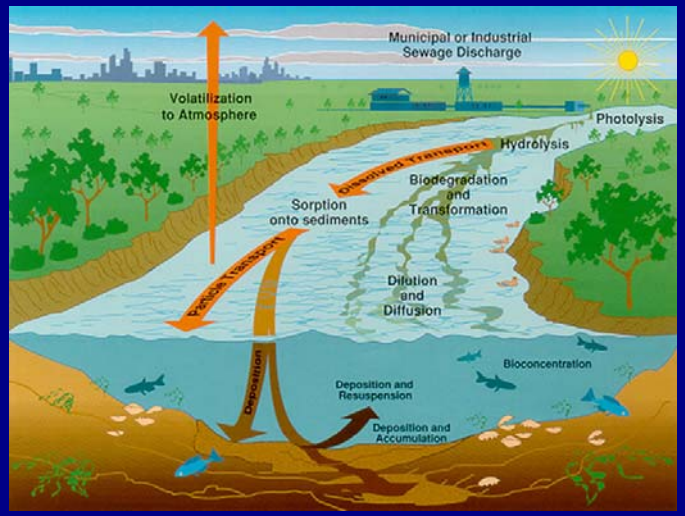
- Found everywhere
- Present in low concentrations and in mixtures
- Most prevalent in municipal wastewater; then streams; less so in drinking water
- Variable removal during treatment
- Pseudo-persistent

What we don’t know

- Ramifications for human health
- Effects of mixtures and chronic, trace-level exposure on aquatic organisms
- What other toxicological endpoints and tests need to be investigated?
- What’s the contribution of EMCs to the overall picture of risk?

Ongoing research

- Analytical chemistry
- Source tracking
- Fate and transport, in natural and treatment systems
- Toxological effects



Response by industry

- Alternatives being investigated for halogenated fire retardants
- PPCP companies
  - Synthetic musks
  - Studying different ways to dose, prescribe, and dispense medications

Response by government

- Congress urging EPA to act
- EPA sponsoring research to obtain science needed to act
- States and local governments piloting pharmaceutical take-back or disposal programs
- White House issued “do-not-flush” guidelines for unused meds

Implications for managers

- Public is concerned about the possibility of EMCs in drinking water
- Public is confused about drug disposal options and consumer options
- Contaminant Candidate List

Closing thoughts

- Opportunities abound for
  - Interdisciplinary collaboration
  - Engaging and informing the public and law-makers

"We have met the enemy, and he is us."
--Pogo

Where to get more information

- USGS Toxics Program http://toxics.usgs.gov/regional/emc/index.html
- EPA's PPCP site http://www.epa.gov/ppcp/
- USGS in North Carolina http://nc.water.usgs.gov/