CONTAMINANTS OF EMERGING CONCERN

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Clean Water Council
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What is the Concern?

- Chemicals we’ve never heard of are showing up in lakes, streams, even drinking water
- New health effects at lower levels
- No one seems to agree on the health risks from current exposures

Result: fears, concerns, reactions
What is the Concern?

- We use a lot of chemicals
- We are better at looking for and finding chemicals
- We have new ways to measure toxicity
- We have toxicity data on a limited number of chemicals (and even fewer health-based guidance values)
When does Concern Emerge?

- When chemicals are being found and people are exposed…

  - AND -

- There is insufficient information to know how the exposures potentially affect people’s health
Why this is Important: the PFC Story

• In the early 2000’s, neither MDH nor MPCA were aware of perfluorochemicals (PFCs)
• 3M very involved in their production
• New class of environmental contaminants with unique properties
• Very little information available on their toxicity, analysis, or environmental fate and transport

PFOA

F F F F F F F O
F—C—C—C—C—C—C—C—C—OH
F F F F F F F

PFOA
Emerging Occurrence in the East Metro

• 2002: 3M discloses that PFC wastes were disposed of at sites in Washington County
• 2003 and 2004: Sampling of private wells and public systems shows PFC contamination
• 2005: PFCs found to be widespread
Large PFC Plumes

Over 100 square miles
- 4 major aquifers
- 8 municipal systems
- >1,000 private wells
- ~150,000 people exposed

PFBA most widespread
More PFBA in source areas
More mobile

Where should we be worried?
What concentrations are a concern?
Emerging Guidance Values

- MPCA first requested MDH to develop health-based guidance for PFCs in water in 2002
- Very little information in literature at first
- Evolving literature resulted in updated guidance values (no federal standards available):

<table>
<thead>
<tr>
<th>Year</th>
<th>PFOA</th>
<th>PFBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
<td>7 ppb</td>
<td></td>
</tr>
<tr>
<td>2007</td>
<td>0.5 ppb</td>
<td>2005: 1 ppb</td>
</tr>
<tr>
<td>2008</td>
<td>0.3 ppb</td>
<td>2008: 7 ppb</td>
</tr>
<tr>
<td>2011</td>
<td></td>
<td>2011: 7 ppb</td>
</tr>
</tbody>
</table>

- Complicated public health messages
TO THE “MDH” WHO SAYS OUR WATER IS SAFE TO DRINK!

Yeah, to the “MDH…” you go first.

Minnesota Dept. of Health:
“Very little PFBA in Woodbury’s drinking water.”

Woodbury Bulletin
Emerging Issues and Concerns

New tools are required:

• For interpreting human health consequences of newly recognized water exposures

• For understanding human exposures
  • Relative contribution that water exposures makes to total exposure must be understood
Why this Initiative?

• Longstanding concerns/need to be proactive rather than reactive
• New concerns about studies of chemicals in waters of the state and in people
• Passage of the Clean Water, Land & Legacy Amendment provided opportunity
• CEC Program supplements (and does not replace) mandated work to provide guidance for health risks from contaminants in groundwater
MDH Health Risk Assessment

• Health Risk Limits
  • “Traditional” contaminants already detected in groundwater
  • Includes naturally occurring substances
  • Rule based; revised every few years
  • Requested and used by Environmental Agencies in cleanup and regulatory decisions

• Contaminants of Emerging Concern
  • Substances that have been released to or detected in Minnesota waters (surface or groundwater) or
  • Have the potential to migrate to Minnesota waters
  • Nomination process
  • Used to guide research and education
Program Process

- Step 1: Nominations
- Step 2: Eligibility
- Step 3: Toxicity and Exposure Screening
- Step 4: Risk-based Selection
- Step 5: Guidance Development
- Step 6: Outreach Materials Development
Step 1: Nomination Process

• Nominations received from
  • State agencies
  • MDH staff
  • Informed stakeholders
  • Public Advisory Forum meetings
  • Web-based year-round nominations (www.health.state.mn.us/divs/eh/risk/guidance/dwec/nominate.cfm)
Nominated Chemicals: Categories
(n=66, through March 2013)
Substances Found in Minnesota Waters

Pharmaceuticals/Medications
- Acetaminophen
- Alprazolam
- Carbamazepine

Other
- Bisphenol A
- Dibutyl phthalate
- Di(2-ethylhexyl)phthalate

Hormones
- Estrone
- 17-alpha Ethinylestradiol
- 17-alpha Estradiol
- 17-alpha Dihydroequilin
- 17-beta Estradiol

Alkylphenols
- Nonylphenol
- Nonylphenol monoethoxylate
- Nonylphenol diethoxylate
- Octylphenol

Personal care products
- Triclosan
- Triclocarban
- Deet

Illicit drugs
- Cocaine
- Benzoylcegonine

Sample of substances reported by USGS and/or MPCA in recent reports
Highlighted substances have been nominated to the CEC program for evaluation
Step 2: Eligibility Determination

- Does it meet our CEC definition?
- Consult with state & federal agencies
- Professional judgment (occurrence?; “new” information?; etc.)
- 11 nominations found ineligible
  - No new data to warrant CEC review (could be reviewed under HRL program)
  - Lack of information from nominator
  - Deferred to federal review
Step 3: Screening Process

- Rapid Assessment
- Toxicity
  - Hazard potential
  - Feasibility (adequate available data)
- Exposure
  - Exposure potential
Step 4: Risk-Based Selection

- Based on toxicity and exposure potential identified in Step 3: Screening
- Developed using input from task group
Step: 5 Guidance Development

- Same peer-reviewed methodology that is used in HRL rule
Step 6: Materials Development

Drinking Water Contaminants of Emerging Concern Program
A Minnesota Clean Water Fund Initiative
2012-2013 Biennium, Interim Report
Minnesota Department of Health
August 2012

The Clean Water Fund: Protecting and restoring Minnesota's waters for generations to come.

At a Glance

Microcystin-LR is...
- A classical produced by cyanobacteria ("blue-green algae") that can grow in lakes and rivers.

Microcystin-LR enters your body from...
- Drinking untreated water affected by cyanobacteria.
- Contact with water affected by cyanobacteria.
- Possibly from dietary supplements made from algae.

Your exposure to microcystin-LR can be reduced by...
- Keeping yourself and your pet away from lakes and rivers with green scums. Wash thoroughly if you come in contact with these waters.
- Use caution and consult your doctor about risks when considering whether to take algae supplements.
- Eat fish caught from lakes with active algal blooms in moderation.

Microcystin-LR in drinking water is safe if...
- The level is lower than the MDE guidance value of 0.04 ppb.

September 2012
Microcystin-LR in Drinking Water
Nominated Chemicals: Status
(n=66, through March 2013)

- Step 6: Guidance & outreach materials completed (19)
- Step 2: Not eligible (11)
- Step 3: Screening in progress (4)
- Step 3/4: Screening completed; on list for future consideration (28)
- Step 5: Review in progress (4)
Stakeholder Input

• Criteria Prioritization Task Group
  • Changed ways chemicals were selected
  • Advised use of non-mammalian data for assessments

• Communication Task Group
  • Revised information sheets
  • Suggested more holistic presentation of information
  • Advised on outreach and education demonstration grants

• Advisory Forum
  • Advised MDH on use of materials and guidance
Education and Outreach Grants

- 4 grants awarded
  - Ce Tempoxcalli
  - Central Minnesota Water Education Alliance
  - Otter Tail County Public Health
  - River Keepers

- Otter Tail Public Heath
  - Promote and support ongoing prescription drug take backs and hazardous waste collection.
  - Increase the amount of participation and the volume of pharmaceuticals and hazardous waste materials collected.
Example: 1,2,3 - Trichloropropane

- A contaminant of soil fumigants once used in MN; also an organic solvent used in industrial settings
- Found in MN groundwater at closed landfill
- MDH developed an HBV of 0.003 ppb in 2011
- Reporting limits for drinking water samples were typically 0.5 ppb; presence in drinking water could not be ruled out
- CEC program worked with MDH Public Health Laboratory to develop lower reporting limits (0.0007 ppb)
Example: Microcystin

- Ambient/Recreational water quality – Swimming, boating, fishing, livestock, pets
- Produced by cyanobacteria
  - Drinking water quality
  - Surface water sources
  - Groundwater under the influence of surface waters
- No microcystin in MN groundwater to date, but potential exists
- 2012 MDH guidance value developed
Microcystin, continued

- MDH Site Assessment & Consultation Unit: Little Rock Lake
- Shallow, nutrient rich lake in Benton Co.
- Numerous & severe algal blooms
- Potential for impacts to shallow wells
Example: Triclosan / Triclocarban

- Anti-bacterial additives in personal care and cleaning products
- Detected in wastewater and surface water in MN
- Recent information on bacterial resistance and ecological concerns led to legislative hearings and a proposed ban
- Proposed ban did not move forward in part because of ongoing MDH review of triclocarban and availability of HBV for triclosan
Intra-MDH collaboration

- New analytical methods
- New PHL capacity
- Testing of public health messages for private well owners
- Funding for analysis (microcystin in drinking water)
Inter-agency Collaboration

• “Minnesota researchers found 56 chemicals — including cocaine — in the state’s waters, according to two studies released today that raise questions about potential impacts on wildlife and human health.”
Inter-agency Collaboration, continued

- Evaluating human health implications of environmental monitoring
  - DEET: 76% of lakes
  - BPA: 43% of lakes
  - Triclosan: 14% of lakes
- Impact on shallow wells near lakes & rivers?
Inter-agency Collaboration, continued

- MPCA collaboration on holistic messages about environmental impacts
- USGS agreement to share occurrence data
- EPA providing Minnesota with new research on relative toxicity within groups of chemicals
Future Plans and Opportunities

• Continue to
  • Develop guidance for additional CECs
  • Expand analytic capabilities of Public Health Laboratory
  • Integrate environmental and human health information
  • Refine alternative risk assessment methods to speed up evaluation of chemicals and classes of chemicals

• Begin to
  • Use high throughput screening to compare toxicity of chemicals within a class of chemicals
  • Evaluate risk assessment methods for microbial / biological contaminants
CEC Guidance Program Outputs

- Guidance values
- Educational materials
- Alternative risk assessment methods
- Products from outreach/education grants
- Enhanced collaboration at state and federal level
CEC Guidance Program Outcomes

• People’s health is protected:
  • Increased public awareness, knowledge, without undue alarm
  • Informed public debate and community decision making
  • Meaningful actions by communities and individuals

• Drinking water is protected:
  • Enhanced source water protection activities
  • Wise investment of public resources
  • Anticipatory actions for public water suppliers/private well owners
Questions?
Thank you

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Contaminants of Emerging Concern

Silent Spring
by Rachel Carson
Drawings by Lois and Louis Darling
Houghton Mifflin Company Boston
The Riverside Press Cambridge
1962

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New E.P.A. Scrutiny Is Set for a Chemical in Plastics

By JOHN M. BRODER
Published: March 29, 2010

WASHINGTON — The Environmental Protection Agency plans to add bisphenol-A, or BPA, a plastic widely used in food packaging and plastic bottles, to its list of chemicals of concern because of potential adverse impacts on the environment and human and animal health.

Bisphenol-A
A list of resources from around the Web about Bisphenol-A as selected by researchers and editors of The New York Times.

The agency will require new studies of concentrations of the plastic in surface water, groundwater and drinking water to determine where it exists in the environment.

Study reports hints of phthalates to boys’ IQs
Researchers link lower IQs in children to some plastics and food packaging.

Our Stolen Future
THEO COLBORN, DIANNE DUMANOSKI, AND JOHN PETERSON MYERS

MAGAZINE OF THE SOCIETY FOR SCIENCE & THE PUBLIC

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Drugs on Tap
By Janet Raloff
Web edition: Monday, April 5th, 2010

By Janet Raloff
Web edition: Monday, March 10th, 2008
Toxic Substances Control Act - TSCA

- 1976, Federal law on toxic chemical regulation
- Regulates introduction of new chemicals for use in manufacturing
- Is an Inventory - chemical is safe until proven otherwise
- 84,000 chemicals on list
- 62,000 on list were grand-fathered in
Commercial chemicals in US

Pharmaceuticals & cosmetics
~12,000

Polymers
~40,000

Industrial chemicals
~42,000

Not included:
• Minor use products (<4.5t/y)
• Degradation products
• Byproducts/impurities
• Isomers/congeners
• Imports
What is actually regulated?

- CERCLA 276
- RCRA 140
- CWA 126
- SDWA 90
- CAA 187

~ 370 chemicals
Global Distributions of Toxic Chemicals

The “Dirty Dozen”

- PCBs
- DDT
- Dioxins and furans
- Chlorinated pesticides
Chemicals of Emerging Concern (CECs)

- Those previously unidentified due to advances in analytical techniques
- Those previously identified but with new effects of concern
- Newly marketed chemicals

*Many are not yet regulated as contaminants*
How many CECs are out there…?

Derek Muir and Phil Howard (2006) –

- ...from > 100,000 compounds in commerce

- ...from ~22,000 persistent and bioaccumulative compounds in commerce

- estimated 610 of potential concern
How widespread is the problem?

Endocrine disrupting compounds and other pharmaceuticals observed in streams and wastewater treatment plant discharges in the US, Europe, & Asia
Organic Contaminants in US Surface Waters
Top 11 of 55 compounds
Median concentrations generally <10 ng/L

- Atenolol - betablocker
- Atrazine - herbicide
- Carbamazepine - anticonvulsant
- Estrone - hormone
- Gemfibrozil - antilipidemic
- Meprobamate - antianxiety
- Naproxen - anti-inflammatory
- Phenytoin - anticonvulsant
- Sulfamethoxazole - antibiotic
- TCEP - flame retardant
- Trimethoprim - antibiotic

Benotti et al. ES&T 2009
Where do they come from?

- Food containers
- Personal care products
- Detergents and cleaners
- Drug disposal
- Industrial discharge
- Agriculture
CECs accumulate in WWTP

- Wastewater Effluent
  - Estradiol & Birth Control Pills
  - Nonylphenol from detergents
  - Bisphenol A and phthalates from plastics
  - Triclosan from household cleaners
  - Musks from personal care products
Why should we be concerned?
Evidence for wildlife effects
Evidence for effects

Intersex found at 31% of sites

Hinck et al. 2009 Aq Tox
Challenges

- Measurement and assessment tools
- Source attribution
- Exposures to humans and fish & wildlife
- Population effects – fish & wildlife
- Human effects – subtle effects, many confounders
- Reduction and removal strategies – moving “upstream”
Risk Evaluation

Source: EPA Office of Research and Development.
Risk Evaluation

Source: EPA Office of Research and Development.
Risk Evaluation

Source: EPA Office of Research and Development.
Challenge: linking biological response to population effects

- molecular
- cellular
- tissue
- individual
- population

Bioassays, microarrays, “-omics”
Whole organism lab assays
Weight of evidence

Increasing Ecological Relevance

Increasing Diagnostic (Screening) Utility

adapted from Miracle and Ankley 2005
Challenge: confounding issues in toxicity assessments

- Any part of cascade can be affected

Glands direct hormone production \(\rightarrow\) Hormones bind to receptor

\[\text{Up-regulate or down-regulate genes}\]
\[\text{mRNA transcription}\]
\[\text{Protein production or alteration}\]

www.ehormone.tulane.edu
Challenge: confounding issues in toxicity assessments

- Any part of cascade can be affected
- Non-linear dose responses possible
Challenge: confounding issues in toxicity assessments

- Any part of cascade can be affected
- Non-linear dose responses possible
- Different doses can lead to different effects
- Different species have different sensitivities and different effects to same exposures
- Different points in life cycle of same species have different sensitivities and different effects to exposure
- Exposure during development can lead to adult disease
Examples of Developmental Origins of Health and Disease

Developmental Exposures

Learning Differences/Behavior
- Asthma
- Increased Sensitivity to Infections
- Testicular Dysgenesis Syndrome

Infertility

Obesity

Altered Puberty

Fibroids
- Premature Menopause

Atherosclerosis
- Cardiovascular Disease

Breast Cancer

Prostate Cancer
- Alzheimer's
- Parkinson's

AGE

2  12  25  40  60  70
Challenge: confounding issues in toxicity assessments

- Any part of cascade can be affected
- Non-linear dose responses possible
- Different doses can lead to different effects
- Different species have different sensitivities and different effects to same exposures
- Different points in life cycle of same species have different sensitivities and different effects to exposure
- Exposure during development can lead to adult disease
- Some effects are transgenerational
Epigenetic Changes

**Normal processes**
- Development
- Cell differentiation
- Aging

**External influences**
- Environmental exposures
- Nutrition
- Chemical toxins
- Metals
- Mediators of stress
- Drugs of abuse
- Infection (including HIV)

**Adverse health outcomes**
- Cancer
- Cardiopulmonary disease
- Autoimmune disease
- Obesity
- Diabetes
- Neurodevelopmental disorders
- Schizophrenia
- Addiction
- Depression

**GENOME**

**EPIGENOME**

**DISEASE**
MWSF Recommendations

Strategy 1: Move upstream of hundreds of potentially harmful, trace level contaminants entering from different sources

**Action Plan:** Establish MN as Green Chemistry Leader

- Promote Green Chemistry and Manufacturing Act
- Promote Governor Executive Order to create Green Chemistry Cluster in MN (EI Multi-stakeholder Comm.)
- Promote policies that provide economic incentives for green chemistry
Change the Paradigm: move upstream

Product R&D

Product Manufacture

Consumer Use

Waste Disposal
MWSF Recommendations

Strategy 2: Manage the CECs already in water

- **Rec:** Develop systematic science-based management and policy framework that uses multi-pollutant approach
- **Rec:** Expand MDH drinking water CEC program to include other routes of exposure
  - **Rec:** Prioritize treatment plants and what are best treatments
  - **Rec:** Develop comprehensive policy for drug collection and disposal
Timeline and Impact

Impact Matrix

- C.1.a: Green Chemistry Act
- C.2.a: develop framework for managing CECs
- C.2.b: expand MDH CEC program
- C.2.c: pharmaceutical disposal
- C.2.d: treatment technologies
- C.3.a: state policy for pathogens and beaches
- C.3.b, c: pathogen indicator and source tracking research

Cost

Impact

H

M

C.1.a, C.3.a, C.3.b

C.3.c

L

C.2.a, C.2.b, C.2.c, C.2.d

L

M

H
MPCA studies find unregulated chemicals widespread in lakes and rivers

St. Paul, Minn. — Two studies released today by the Minnesota Pollution Control Agency (MPCA) confirm that a wide variety of unregulated chemicals are ending up in Minnesota’s lakes and rivers. The chemicals, including pharmaceuticals and personal care products, are of concern because many have properties that can interfere with the functioning of hormones in animals and people.

Flame Retardants Linked to Lower IQs, Hyperactivity in Children

A new study confirms that exposure in the womb to fire-busting chemicals in furniture and carpet pads may hinder child development

By Dina Fine Maron

‘Chemicals of high concern' found in thousands of children's products

Baby bibs. Ethylene glycol in dolls. Methyl ethyl ketone in clothing. Antimony in high chairs and booster seats. Parabens. Analysis of thousands of reports from America’s largest companies shows that toys and other children’s products contain unexpected ingredients that will surprise a public concerned about exposure. The reports were filed by 59 large companies to comply with an unprecedented state law.
MPCA Monitoring

Surface water monitoring

- Long term repeating five-year cycle of probabilistic surveys to provide data sets for trend analysis, done with EPA national lake and stream surveys

Groundwater monitoring

- Collaboration with the U.S. Geological Survey (USGS)
- Approximately 40 wells a year for Endocrine Active Compounds (EACs) and other Contaminants of Emerging Concern (CECs)
Surface Water Analytical/Methods

2008 Statewide Survey
- 11 lakes and 4 river sites representing different land uses
- Partnered with USGS and St Cloud State University
- 110 chemicals analyzed by USGS

2010 Flowing Waters Probabilistic Survey
- 150 randomly selected sites
- 18 pharmaceuticals and personal care products analyzed by MDH

2012 Lakes Probabilistic Survey
- 50 lakes randomly selected
- 125 chemicals including pharmaceuticals, personal care products and EACs, analyzed by Axys
Levels in Surface Water

Pharmaceuticals

Swine antibiotic carbadox – 28 % lakes, up to 121 ppt
Antidepressant amitriptyline – 28 % lakes, up to 4 ppt
Levels in Surface Water

Personal care products

DEET insect repellent – 76% lakes, up to 125 ppt
Common disinfectant triclosan – 13 % lakes, up to 12 ppt
Endocrine active compounds

- Bisphenol A – 43% lakes, up to 15 ppt
- Nonylphenol – 10% lakes, up to 20 ppt
- Androstenedione – 30% lakes, up to 7 ppt
Levels in Surface Water

CECs detected ubiquitously at low levels
Insufficient data to establish trends
Land use is important
Surface and groundwater point sources can be a significant source
Air deposition can be a significant source
Groundwater Analytical/Methods

2009-2010, 40 wells in non-agricultural areas
35 wells in shallow sand and gravel aquifers
5 wells in deeper Prairie du Chien- Jordan
Lab analysis by USGS for 100 CECs
Groundwater Analytical/Methods
Levels in Groundwater

EXPLANATION
- No detections
- One or more chemicals detected (the number detected is shown next to the well)
Levels in Groundwater

Low frequency and low levels of detection, even though wells more likely to be contaminated were targeted.

CECs present in 13 of the 40 wells monitored.

EACs 3 of the 40 wells.

GW affected by landfill leachate had the largest number of detections and highest total concentrations.
Levels in Groundwater

No concentrations exceeded any applicable health-guidance values
80% of detections measured at $\leq 1$ ppm
50% of detections measured $< \text{less than the laboratory reporting limit}$
Are CECs at a Level of Concern?

No established surface water regulatory thresholds

• Can only compare levels of what we have seen to academic studies that show effect
• Studies have shown fish predatory responses are slowed after exposure to mixture of pharmaceuticals
• Similar studies for other compounds

Groundwater values below health risk levels
Developing Actionable Levels

Lack of aquatic life regulatory thresholds
Proposed initiative to screening values/benchmarks
Utilize available information about toxicity and endocrine impacts
Complement MDH CEC work that focuses on human health exposure via drinking water
Develop protocol, 2 benchmarks in year 1, and 8 in year 2
Gap 1: Information about ecosystem/aquatic life and human health effects aka what levels are of concern?

Initiative 1: 325K to develop screening values/benchmarks to quantify risks of specific CNCs to human health and aquatic life. Complement and benefit from MDH’s work (which focuses on human exposure via drinking water) to evaluate the effects of CNCs on beneficial uses of surface waters, such as effects on aquatic life communities.
Impacts to water quality and fish communities

Minnows exposed to EACs had slower response times and were more likely to be eaten.
Exposed fish spawned later and produced fewer eggs.
Fewer young and young are more likely to be eaten will shrink population.
Fathead minnow population crashed when Canadian researchers exposed an entire lake to EACs.
EACs exposure can lead to feminization of male fish.
EAC exposure can cause fish to become more aggressive.
Ongoing studies in Minnesota lakes to determine how much EACs affect spawning behavior.
Questions?

Katrina Kessler
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2008 Statewide surface water study

2009 -2010 Groundwater study

2010 Rivers and streams study

2012 Lake study