Emerging Environmental Contaminants

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Emerging Contaminants

- Sucralose (Splenda !)
- Perfluorinated Chemicals (e.g., PFOA and PFOS)
- Pharmaceuticals
- Nanomaterials
- DBPs (including NDMA and nitrosamines)
- Pesticide reaction/degradation products
- Brominated flame retardants (PBDEs)
- Perchlorate
- Algal toxins
- Benzotriazoles
- Dioxane
- Sunscreen chemicals (UV filters)
- Gasoline additives
- Naphthenic acids
- Hormones
- Pathogens

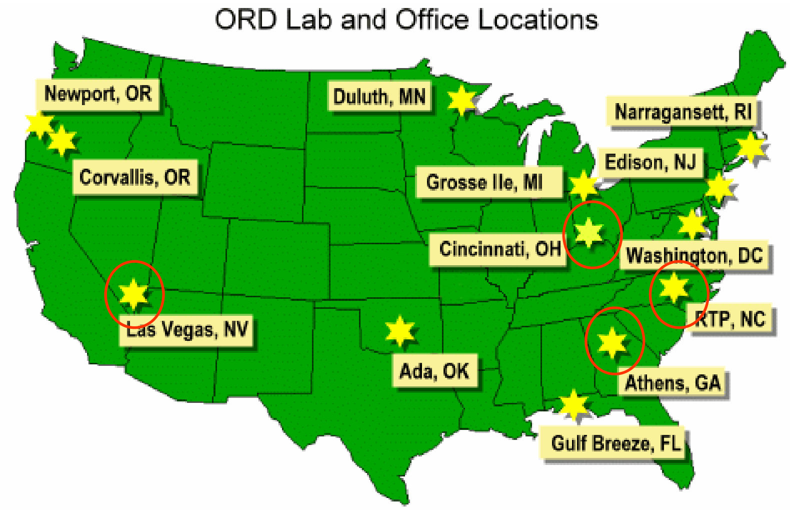
U.S. EPA

Athens, GA

RTP, NC

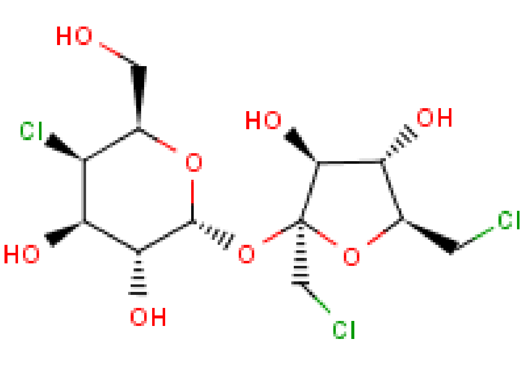
Much of the emerging contaminant research described in this presentation is from EPA's Office of Research & Development's four National Exposure Research Laboratories.

Cincinnati, OH



Las Vegas, NV

Sucralose (Splenda) !



- Artificial sweetener; widely used; very stable (can bake with it)
- Large European study (120 samples from 27 countries)
  Loos et al., *J. Chromatogr., A* 2009, 1216, 1126-1131.
- Up to 1 µg/L in river waters; extremely persistent
- Also reported in the United States in marine and coastal waters: Mead et al., *Marine Chemistry* 2009, *116*, 13-17.

- Up to 118 µg/L in wastewater effluents
  Up to 372 ng/L in Cape Fear River Estuary (NC)
  Up to 67 ng/L in Gulf Stream
  Up to 392 ng/L in Florida Keys
- Persistent in coastal/marine waters
- Deep water levels similar to surface levels
- Significant amount is not degraded microbially; oceanic currents may distribute globally
- Other artificial sweeteners also now being measured

PFOS/PFOA

PFOS:
Perfluorooctanesulfonate

$CF_3—(CF_2)_7—SO_3^-$

PFOA:
Perfluorooctanoic acid

$CF_3—(CF_2)_6—COOH$

- Used to make soil-, stain-, grease-, and water-resistant coatings that are widely applied to fabrics, carpets, cookware, paper (microwave popcorn bags)
- Persistent, bioaccumulative, toxic (including developmental), ubiquitous contaminant
- PFOA and PFOS now on new CCL-3
- PFOS not manufactured in North America anymore;
- environmental levels decreasing
- Eight manufacturers just phased out PFOA by 95% (2010)

CCL-3: www.epa.gov/safewater/ccl

PFOA

Ever wonder why grease doesn't come through paper wrapper?

From Athens Sunday paper on Jan. 8

PFOA

Questions and Concerns

- Why is it in the bloodstream of almost everyone measured?
- Where is it coming from? How is it transported?
- Why is found in biota in the Arctic?
(Up to 3112 ng/g in polar bears from Arctic—can be at greater levels than PCBs)

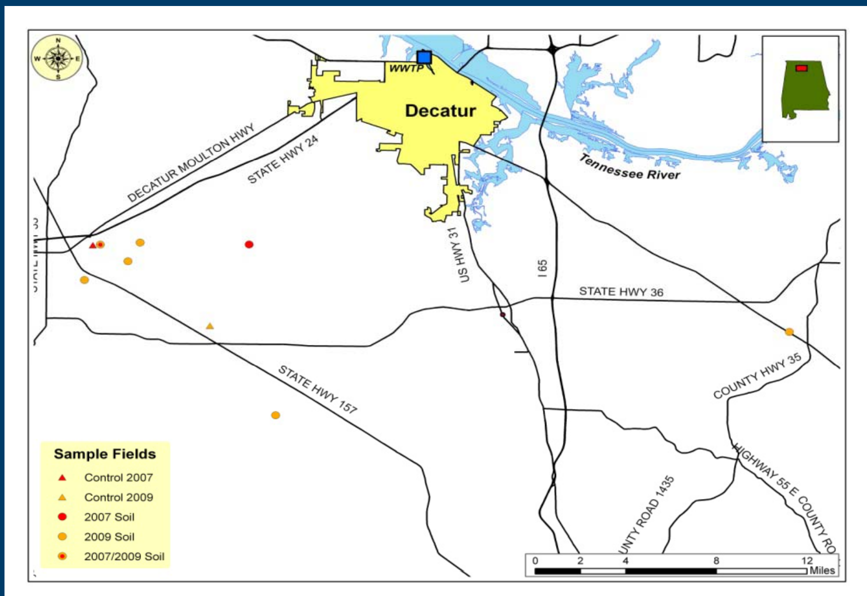
Hypothesis: telomer alcohols volatile, transported, oxidized to acid in atmosphere and in the body (Henderson & Smith, *Toxicol. Sci*. 2007, *95*(2), 452). Also recent evidence that PFOA itself is volatile.

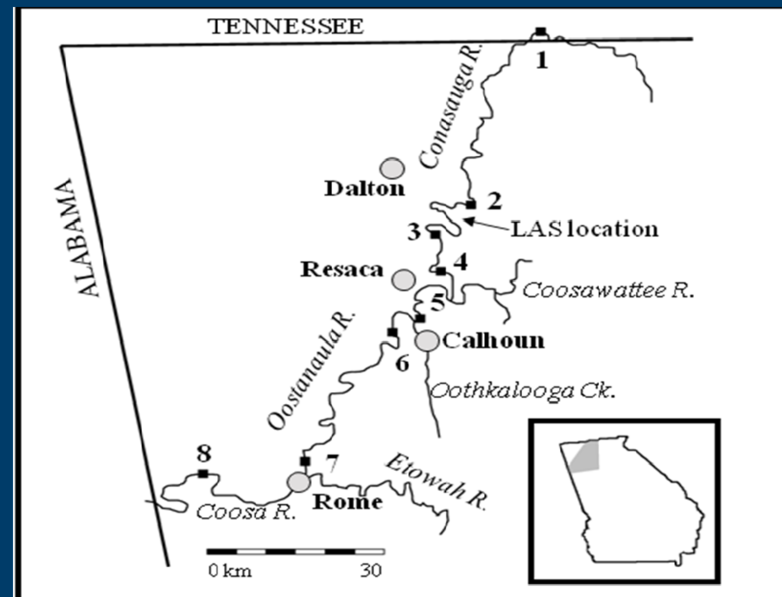
Recent EPA work:

- exploring microbial degradation of fluorotelomer polymers
- investigating sources & sinks for PFOA (including sorption)
- large worldwide occurrence study in soils
- investigating source from sewage sludge used as soil improver
- measuring PFCs in fish

EPA
United States
Environmental Protection
Agency

Measurement in Soil, Water, Sediments, Worms





Site 1: Decatur, AL

- Terrestrial
- Sludge, PFAs elevated ~50x
- Applied ~5000-acres agricultural land
- Sampled surface soil, subsurface soil,
- Plants accumulate lower chain PFAs
  - Yoo et al., ES&T 2011, 45, 7985.

Site 2: Dalton, GA

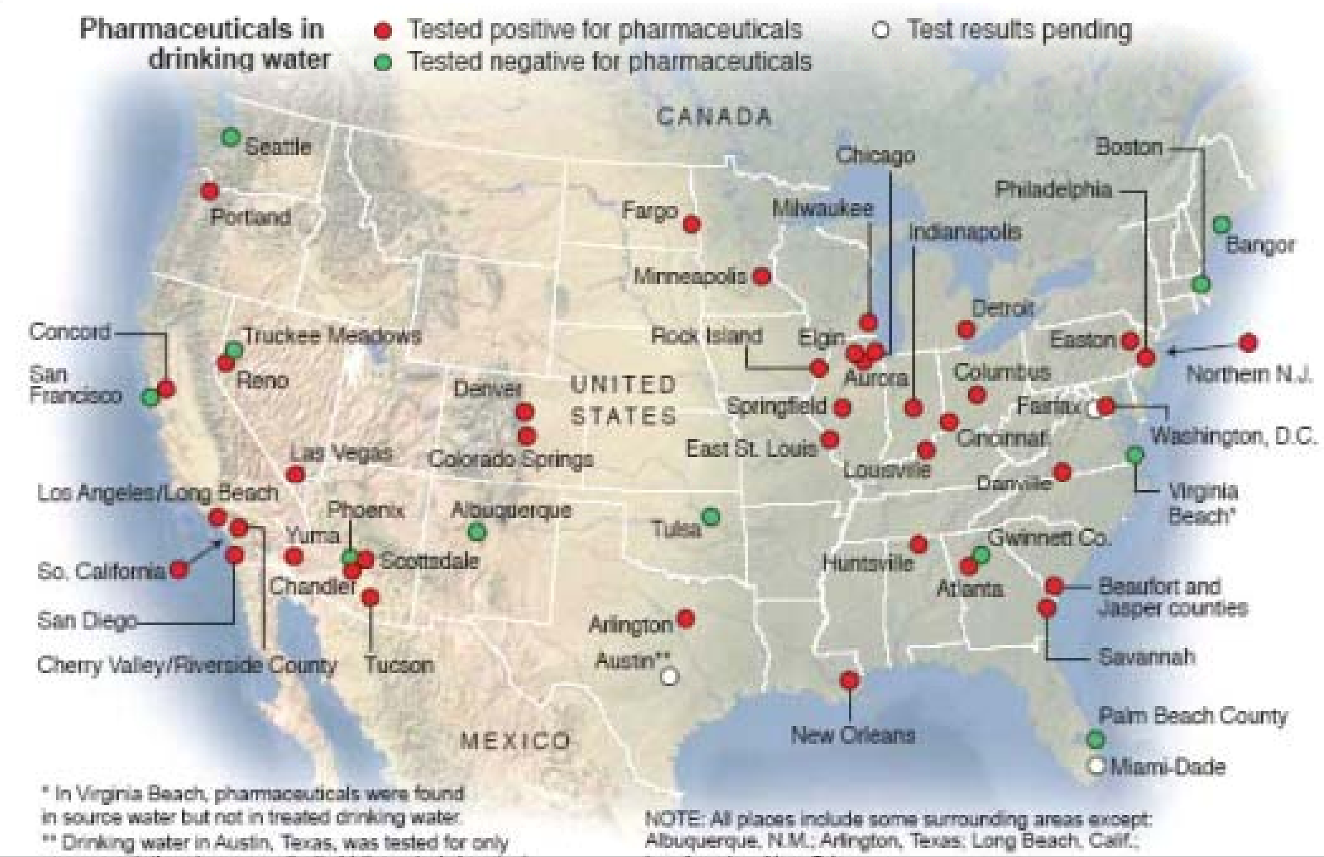
- Conasauga River
- WWTP receiving PFA waste
- Effluent irrigation near river
- Sampled water sediments – upriver & downriver
- Worms exposed to sediments in lab
- Worms accumulate higher chain PFAs
  - Lasier et al., Environ. Toxicol. Chem. 2011, 30, 2194.

Slide courtesy of John Washington, U.S. EPA, Athens

Pharmaceuticals

46 million in U.S. have drugs in drinking water

Testing shows traces of meds in water greater than previously reported



updated 4:29 p.m. ET, Thurs., Sept. 11, 2008

Testing prompted by an Associated Press story that revealed trace amounts of pharmaceuticals in drinking water supplies has shown that more Americans are affected by the problem than previously thought — at least 46 million. That's up from 41 million people reported by the AP in March as part of an investigation into the presence of pharmaceuticals in the nation's waterways.

Pharmaceuticals

Three now included on the CCL-3; will also be included in new Water Quality Criteria

- Potential estrogenic effects on biota (e.g., feminization of fish)
- Vultures: diclofenac poisoning
- Potential antibiotic resistance
- Potential adverse effect on wastewater treatment
- May affect aquatic organism populations (decreased food sources)
- Transformation in drinking water treatment
- EPA Method 1694 (water and wastewater)

Science News

... from universities, journals, and other research organizations

Antibiotic Resistance Genes Accumulating in Lake Geneva

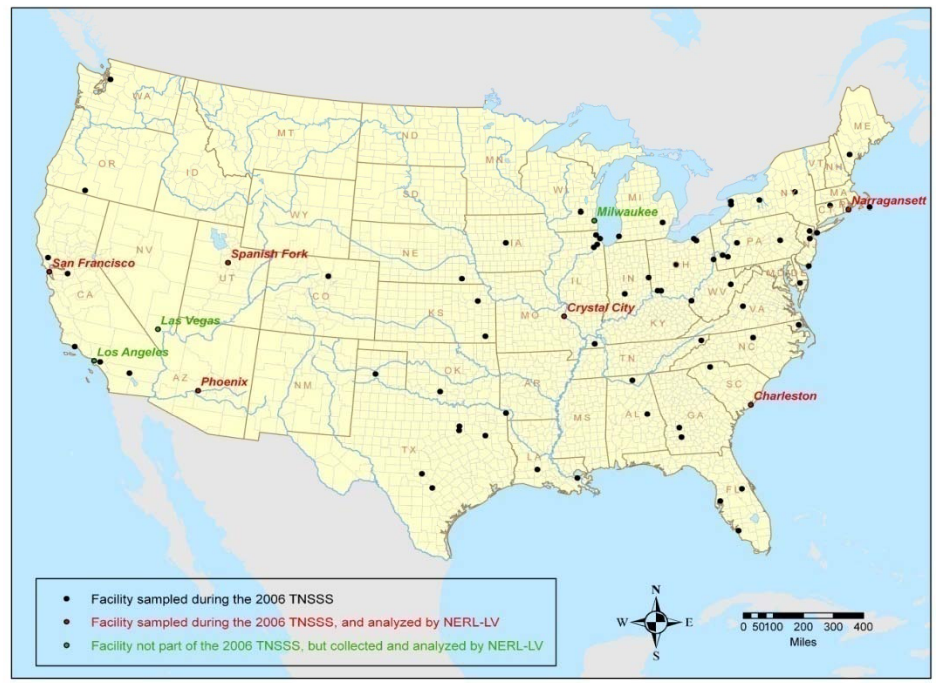
ScienceDaily (Mar. 22, 2012) — Large quantities of antibiotic-resistant bacteria enter the environment via municipal -- and especially hospital -- wastewater streams. Although wastewater treatment plants reduce the total number of bacteria, the most hazardous -- multiresistant -- strains appear to withstand or even to be promoted by treatment processes. This was demonstrated by Eawag researchers in a study carried out in Lake Geneva, near Lausanne.

Pharmaceuticals in Biosolids

Tammy Jones-Lepp

- Sampling – Samples collected from different WWTPs from across the U.S.

- Developed PLE-LC/MS/MS method to measure 6 pharmaceuticals



Results

United States Environmental Protection Agency

Table 4. Concentrations of targeted pharmaceuticals and drugs from nine U.S. WWTPs using PLE 3.

Sample ID	Average amount detected*, ng/g (dry wt)					
	AZI	CLA	CLI	METH	n,n'-DMPEA	PSEU
LVBIO001	150	nd	nd	31	nd	nd
LVBIO002	52	nd	nd	nd	nd	nd
LVBIO003	130	310	2100	nd	nd	nd
LVBIO004	170	nd	nd	nd	630	nd
LVBIO005	200	nd	nd	nd	nd	nd
LVBIO006	53	nd	nd	nd	nd	nd
LVBIO008	180	nd	nd	nd	35	nd
LVBIO009	105	190	nd	nd	nd	140

* (n=2), corrected values from matrix spikes recoveries. nd = not detected. Note: LVBIO007 was not analyzed.

AZI = azithromycin
CLA = clarithromycin
CLI = clindamycin
METH = methamphetamine
DMPEA = dimethylphenethylamine
PSEU = pseudoephedrine

Jones-Lepp et al., Enhanced extraction and detection of macrolide antibiotics and other drugs from a complex environmental matrix: biosolids, manuscript in preparation, 2010.

Emerging Contaminants What are They? Or a Paradigm Shift?

United States Environmental Protection Agency

An Example of a Whole Lake Ethynylestradiol Dosing Experiment at Canada's Experimental Lake Area

Jim Lazorchak, U.S. EPA, NERL, Cincinnati, OH

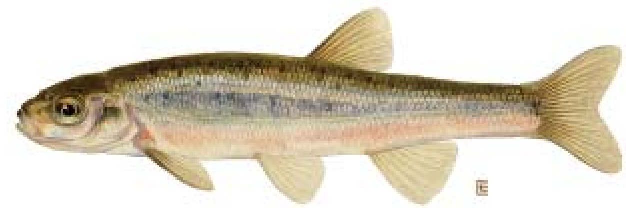
Kidd, Blanchfield, Mills, Palace, Evans, Lazorchak, Flick. 2007. Collapse of a fish population after exposure to a synthetic estrogen. *PNAS* 104, 8897-8901.

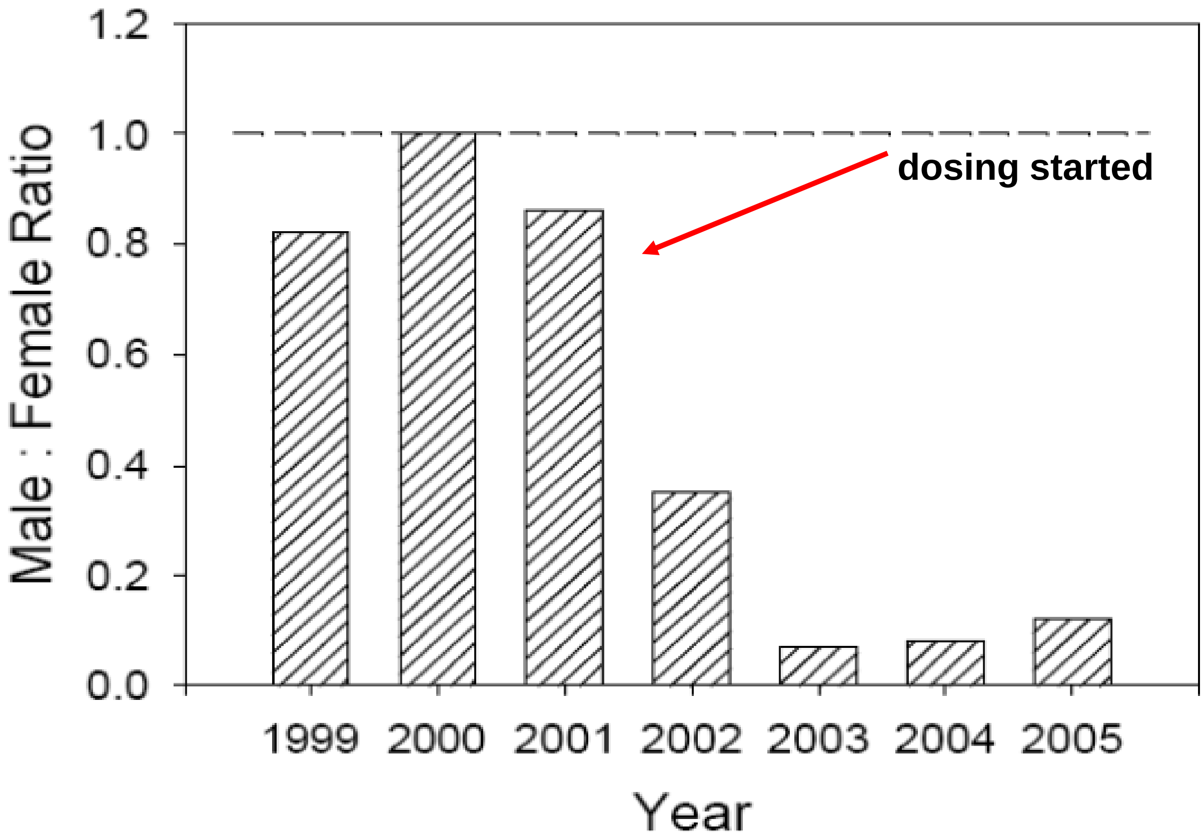
Summary - Fathead Minnow

- Spring 2001 - EE2 additions began
  - Vg gene expression induction in deployed 114 fish in 260 in 24-hrs
  - significant vitellogenin plasma induction after 7 weeks
- Fall 2001 (4 months)
  - proteinaceous accumulation in kidney
  - liver cell size increased
- Spring 2002 (12 months)
  - disorganized testes, immature ovaries
  - decreased spawning aggression, fewer & less-developed eggs
  - reduction in secondary sex characteristics
  - No fish population impacts observed
- Fall 2002 (17 months) - reproductive failure, few age 0 fish
- Spring 2003 (2 years) - only age 2 fish remaining
  - one male found, females with large ovipositors
- 2006 (3 yrs post additions) – Fathead population recovered

United States Environmental Protection Agency

Pearl Dace Sex Ratio





K Mills – FW Inst

Nanomaterials

- Big new area for research
- Major initiative at U.S. EPA to study occurrence, fate, and health effects
- 1-100 nm in size; unique properties
- Examples: Fullerenes (C_{60}), zero-valent iron, TiO_2, nano-silver, nano-gold, functionalized fullerenes (in hollow spheres, ellipsoids, tubes), quantum dots, metal oxanes
- Already used in many consumer products (cosmetics, sunscreens, clothing, paints, tires, tennis rackets, lubricants, electronics, soaps, shampoos, detergents; zero-valent iron used to remediate groundwater)
- Many more products under development (e.g., medical diagnostics, cancer treatment)

Nanomaterials—Ecotoxicological Effects?




- Daphnia magna
  - Acute toxicity (C_{60}, C-nanotubes, nano-TiO_2)
  - Accumulation (C_{60}, nano-TiO_2)
  - Physiological changes (C_{60})
  - Reproductive effects (C_{60})
  - Intake (gold nanoparticles)
- Zebra fish
  - Developmental effects, physiological changes (C_{60}, C-nanotubes)
- Rainbow trout
  - Respiratory toxicity, physiological effects (C-nanotubes)
- Frogs (*Xenopus laevis*)
  - Acute toxicity (C-nanotubes) (but NO genotoxicity found)
- Crustaceons (*Amphiascus tenuiremis, Hyalella azteca*)
  - Mortality, developmental and reproductive effects (C-nanotubes, ZnO, nanosilver)
- Various bacteria, algae
  - Acute toxicity (ZnO, nanosilver)

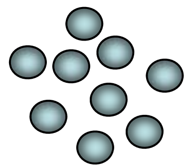
Farré et al., *Trends Anal. Chem*. **2008**, *27*, 991-1007.

But, most studies carried out at very high doses (mg/L)
Not known how they will behave in the environment (will they aggregate and not behave as nanoparticles?
A portion of effects from metal nanomaterials may be due to the release of metal ions (*e.g.*, silver ions)

Biotransformation and Genotoxicity of ZnO and CeO_2 Nanomaterials in Plants

XAS results

ZnO



ZnO NPs were biotransformed

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$Zn(OH)_2$?

Zn^{2+} ?

ZnO

Photo: G. de la Rosa

Jorge Gardea-Torresdey

But CeO_2 unchanged; both genotoxic

López M.L., de la Rosa, G., Hernández, J.A., Michel, H., Botez, C., H. Peralta, J.R., **Gardea-Torresdey, J.L**. ***Environmental Science and Technology***. 2010, 44, 7315–7320.

New evidence for biomagnification

Environ. Sci. Technol. **2011**, *45*, 776–781

Evidence for Biomagnification of Gold Nanoparticles within a Terrestrial Food Chain

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Nanoparticles from the rapidly increasing number of consumer products that contain manufactured nanomaterials are being discharged into waste streams. Increasing evidence suggests that several classes of nanomaterials may accumulate in sludge derived from wastewater treatment and ultimately in soil following land application as biosolids. Little research has been conducted to evaluate the impact of nanoparticles on terrestrial ecosystems, despite the fact that land application of biosolids from wastewater treatment will be a major pathway for the introduction of manufactured nanomaterials to the environment. To begin addressing this knowledge gap, we used the model organisms *Nicotiana tabacum* L. cv *Xanthi* and *Manduca sexta* (tobacco hornworm) to investigate plant uptake and the potential for trophic transfer of 5, 10, and 15 nm diameter gold (Au) nanoparticles (NPs). Samples were analyzed using both bulk analysis by inductively coupled plasma mass spectrometry (ICP-MS) as well as spatially resolved methods such as laser ablation inductively coupled mass spectrometry (LA-ICP-MS) and X-ray fluorescence (μXRF). Our results demonstrate trophic transfer and biomagnification of gold nanoparticles from a primary producer to a primary consumer by mean factors of 6.2, 11.6, and 9.6 for the 5, 10, and 15 nm treatments, respectively. This result has important implications for risks associated with nanotechnology, including the potential for human exposure.

Introduction

Advances in nanotechnology have led to the development of many new consumer products containing nanomaterials and large increases in the mass and volume of several nanoparticles (NPs) produced. Silver (Ag) NPs have been studied extensively, due largely to their demonstrated antimicrobial effects (*1*). This property gives Ag NPs a wide variety of commercial applications, and their production and resultant environmental loading has increased to reflect this (*2, 3*). Titanium dioxide (TiO_2) and zinc oxide (ZnO) NPs are being used in products such as sunscreens, pharmaceuticals, and UV protective coatings (*4, 5*), and as these uses become more widespread, they will inevitably be discharged into the environment in increasing concentrations (*2*).

Between 2005 and 2010, the amount of listed products employing nanotechnology has increased from 54 to 1015 (*3*). As a result, the amount of nanomaterials entering waste streams is increasing steadily (*2*). During wastewater treatment, nanoparticles have been shown to concentrate in the sludge (*2*), 60% of which is applied to agricultural land as biosolids in the U.S. and the majority of Europe (*2*). Probabilistic material flow analysis models have predicted that between 2008 and 2012, the nanomaterials concentrations in sludge-treated soil in the U.S. will increase from 0.1 to 0.5 mg kg^{-1} for TiO_2 NPs, from 6.8 to 22.3 $\mu g\ kg^{-1}$ for ZnO NPs, and from 2.3 to 7.4 $\mu g\ kg^{-1}$ for Ag NPs (*2*).

Plant uptake (*6*), gastrointestinal absorption (*7*), and transmembrane transport of nanomaterials (*8*) have already been demonstrated. In the past, dietary exposure and trophic transfer have proven to be important terrestrial exposure pathways to chemicals such as polychlorinated biphenyls (PCBs), methylmercury, and dichlorodiphenyltrichloroethane (DDT) (*9*). Despite these facts, there has been little research published investigating the trophic transfer of nanoparticles and even less addressing the transfer from plants to animals. In one such study, trophic transfer was reported when freshwater algae (*Pseudokirchneriella subcapitata*) exposed to 10–25 nm CdSe quantum dots were fed to *Ceriadaphnia dubia* (*10*). Another study reported trophic transfer of 6 by 12 nm ellipsoid carboxylated and biotinated CdSe quantum dots from ciliated protozoans to rotifers (*11*). A recent publication presented evidence for the transfer of 21 nm TiO_2 NPs from *Daphnia magna* to *Danio rerio* (zebrafish) (*12*). We have demonstrated the accumulation of Au NPs up to 55 nm in diameter (*9*) and copper (Cu) NPs up to 100 nm in diameter in earthworms from exposure to NP spiked soil (*9, 13*). There are also some studies that provide indirect evidence of trophic transfer. In one such study, researchers presented indirect evidence that gold (Au) NPs transferred from the water column to the marine food web within estuarine mesocosms (*14*). Another study exposed *Caenorhabditis elegans* to ZnO, Al_2O_3, and TiO_2 NPs in the presence of *Escherichia coli* (*E. coli*), which were provided as food (*15*). It is possible that some of the NPs were internalized by the *E. coli* and transferred to the nematodes through dietary uptake.

These initial results suggest that NPs could be available for dietary uptake at lower trophic levels and subsequently transferred through terrestrial food webs. As terrestrial ecosystems are a possible pathway for human exposure (*16*), there is an urgent need to examine the transport and fate of NPs in terrestrial ecosystems under environmentally relevant scenarios. To begin addressing this knowledge gap, we used the model organisms *Nicotiana tabacum* L. cv *Xanthi* and *Manduca sexta* (tobacco hornworm) to investigate plant uptake and the potential for trophic transfer of 5, 10, and 15 nm diameter Au NPs. Au NPs are being used in a variety of applications including the detection and imaging of cancer cells (*17*), pharmaceuticals designed to combat HIV (*18*), and catalysis in fuel cells (*19*). We selected Au for this initial study due to its resistance to oxidative dissolution and release of dissolved Au ions as well as because of its low natural background concentrations (*20*). These properties make Au an ideal model to probe particle specific uptake in complex systems.

Based on previously published results (*6, 7, 9, 10, 12, 13*), we hypothesized that 5–15 nm Au NPs may be transferred through dietary exposure from a primary producer to a primary consumer. We also hypothesize that due to the presence of size selective physiological barriers, such as the plant cell wall, size will be an important factor in plant uptake and potential trophic transfer of Au nanoparticles. Finally,

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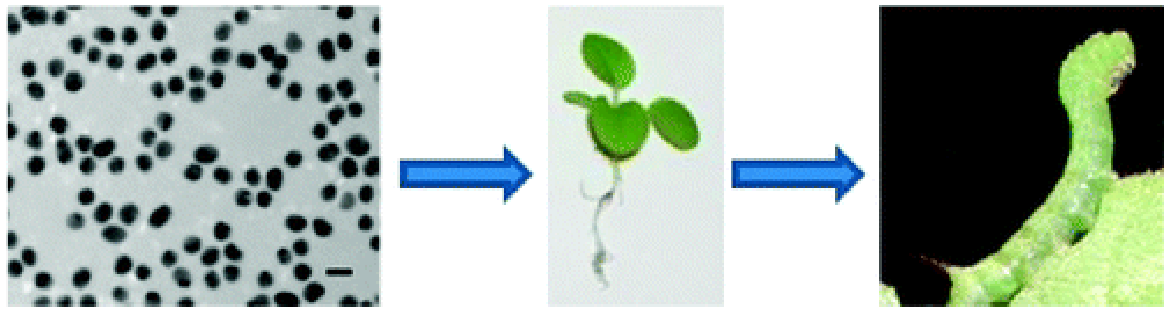
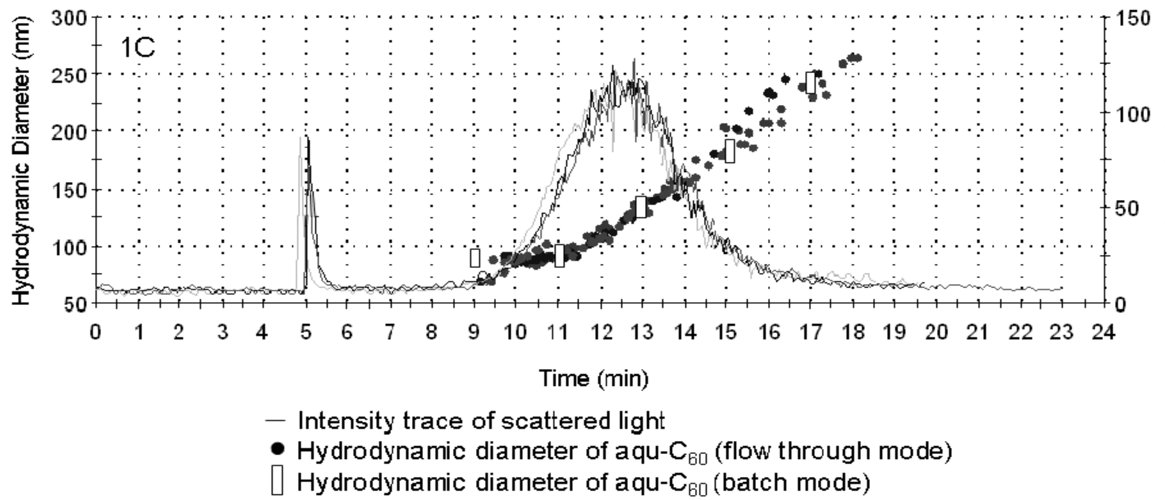
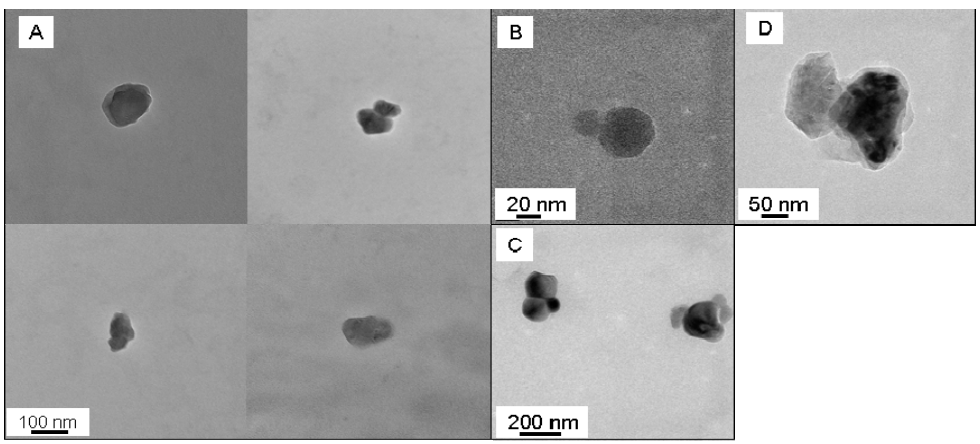
10.1021/es103031a Published on Web 12/03/2010

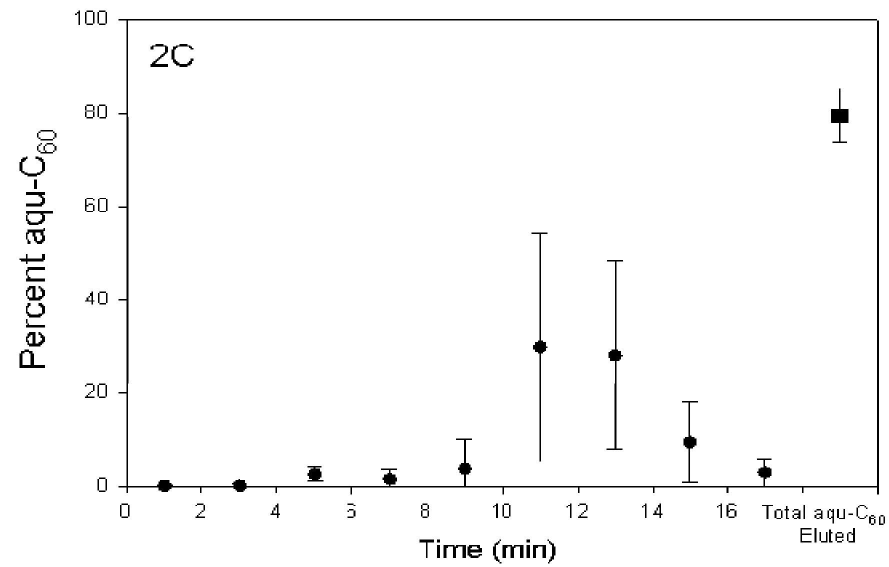


Characterization of Fullerenes with Asymmetric Flow Field-Flow Fractionation (AF4) and LC/APPI-MS

- Aqu/C_{60} aggregate ranged in size from 80-260 nm
- Mass of C60 determined in each fraction by LC/APPI-MS
- Mass balance of 77 ± 5.8 %
- Sizes corroborated by dynamic light scattering in batch mode and transmission electron microscopy
- Use of LC/MS important for specificity—to know which nanoparticles are being measured







Drinking Water DBPs—What are the Issues?

Concern over possible human health risk:

- Epidemiologic studies: risk of bladder cancer; some cause cancer in laboratory animals
- Recent concerns about possible reproductive & developmental effects (from epi studies)

Goal: Comprehensively identify DBPs formed from different disinfectants, test for toxicity, understand their formation, minimize or eliminate in drinking water

DBPs Regulated by the U.S. EPA

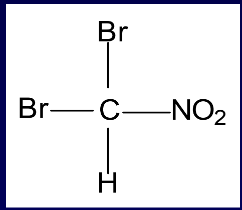
DBP	MCL (µg/L)
Total THMs	80
5 Haloacetic acids	60
Bromate	10
Chlorite	1000

But more than 600 DBPs have been identified

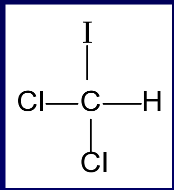
Little known about occurrence & toxicity of unregulated DBPs

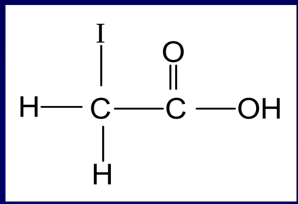
Emerging DBPs

- Halonitromethanes (up to 3 ppb; highly genotoxic); new *in vivo* effects; increased with preozonation

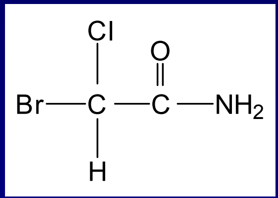


- Iodo-THMs and Iodo-Acids (iodo-THMs up to 15 ppb; iodo-acids up to 1.7 ppb; both classes highly cytotoxic or genotoxic); increased with chloramination
  Richardson et al., *ES&T*, 2008, 42, 8330.

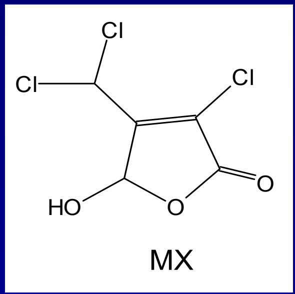




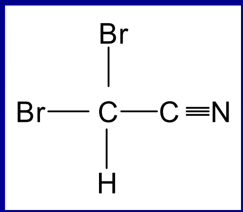
- Haloamides (up to 14 ppb; highly genotoxic) may be increased with chloramination



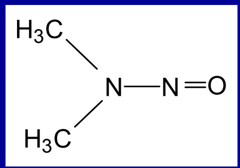
- Halofuranones (up to 2.4 ppb for total MX analogues; genotoxic, carcinogenic); chloramination can also form



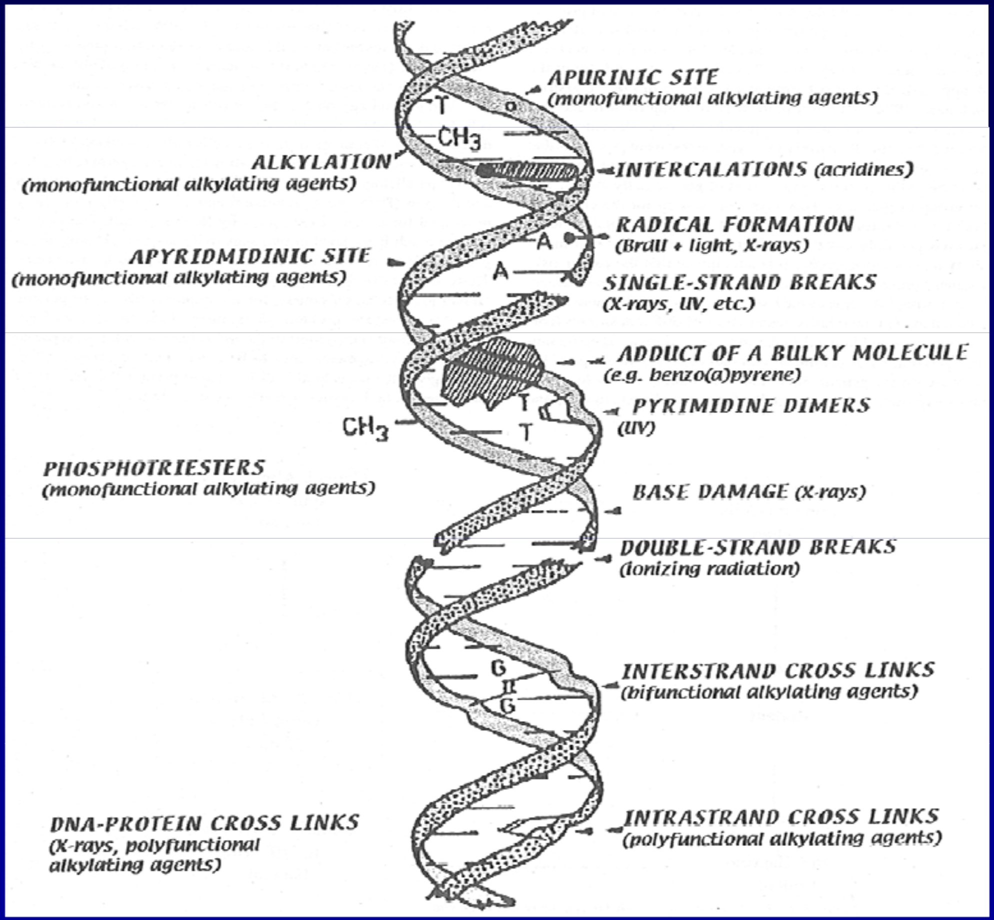
- Haloacetonitriles (up to 41 ppb; ~10% of THM4; genotoxic, cytotoxic); may be increased with chloramination

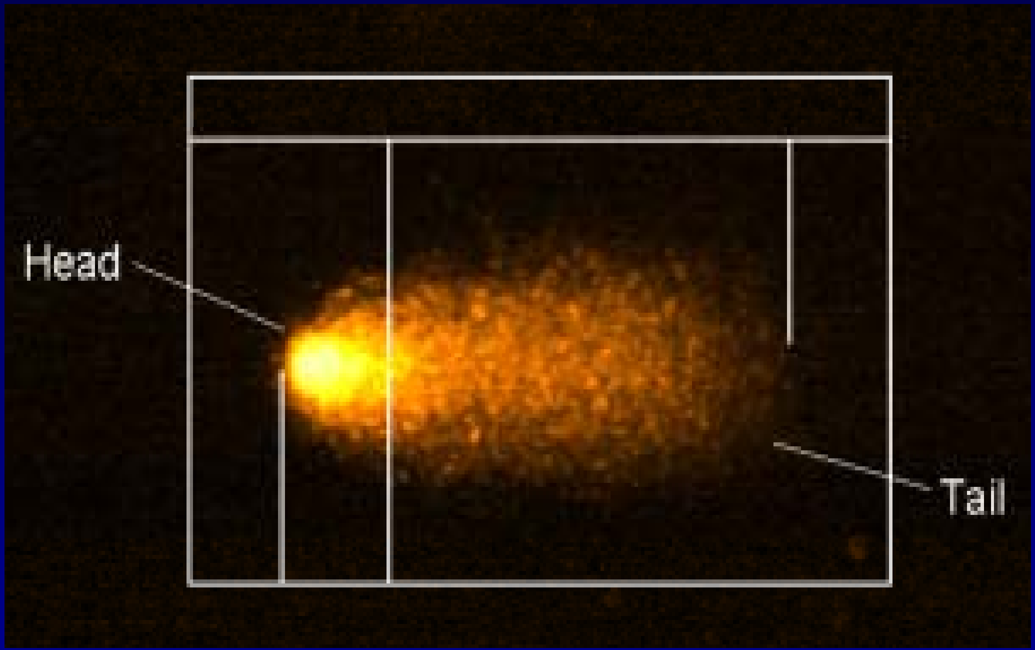


- Nitrosamines (up to 530 ppt; probable human carcinogens); increased with chloramination
  EPA plans to regulate group of nitrosamines



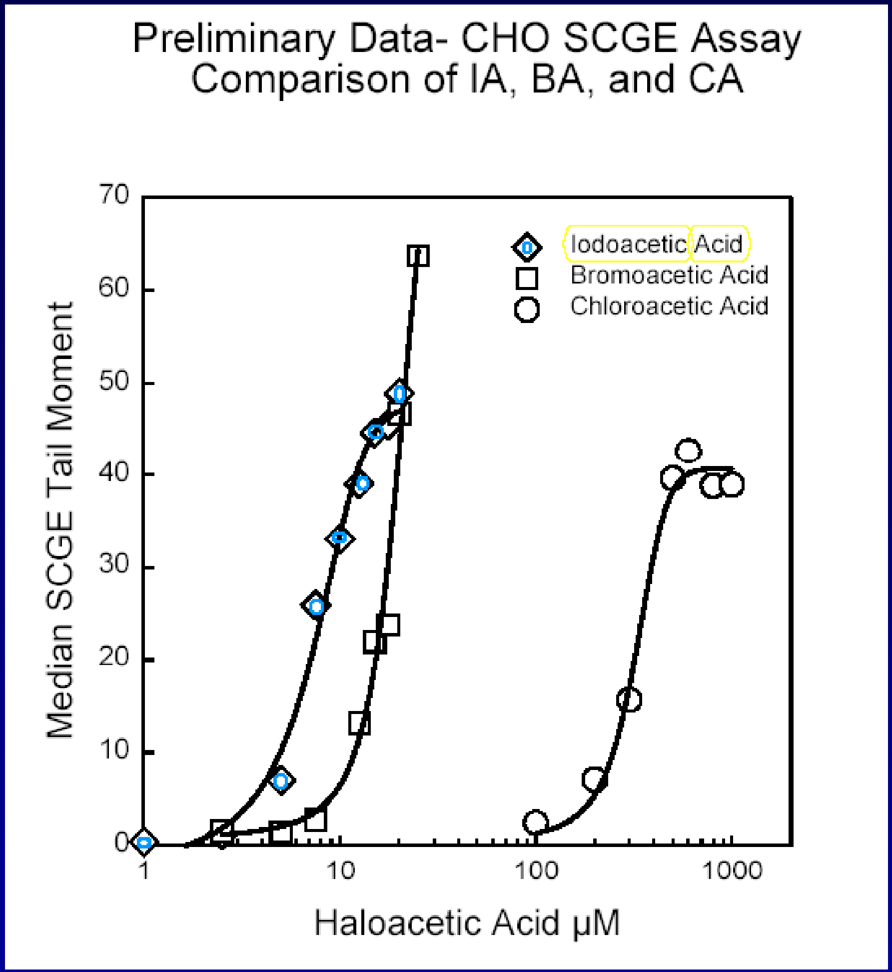
Genotoxicity: Comet Assay





The tail moment is the integrated value of DNA density multiplied by the migration distance. The % tail DNA is the amount of DNA that has migrated into the gel from the nucleus.

Genotoxicity of Iodoacetic acid

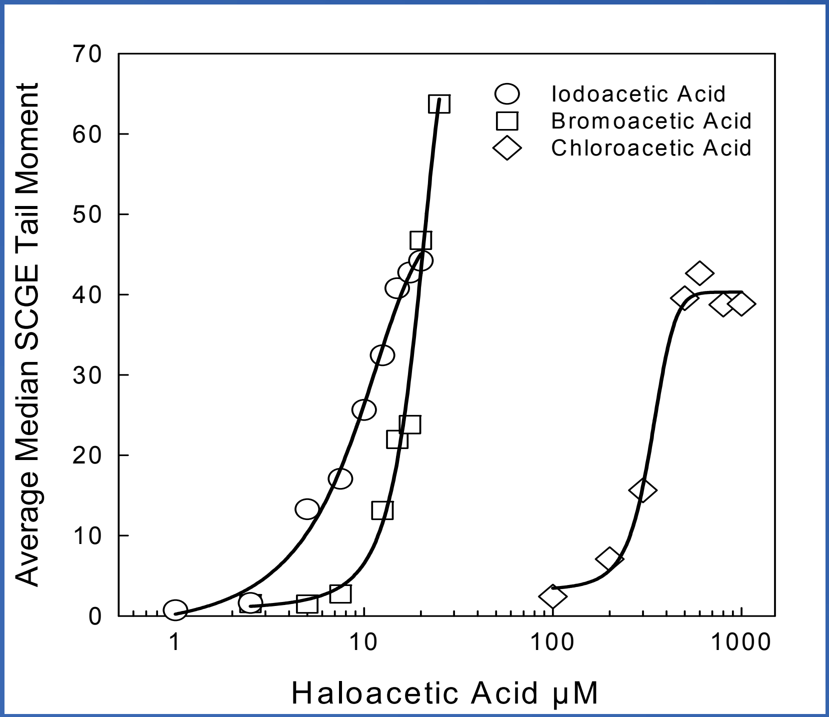


Plewa et al., *Environ. Sci. Technol*. 2004

IA also caused developmental effects in mouse embryos (Hunter et al., 1995)

Iodo-acid/iodo-THM occurrence study: Richardson et al., *ES&T*, 2008, 42, 8330.
Also reports genotoxicity & cytotoxicity of other iodo-acids and iodo-THMs

New Human Cell Results

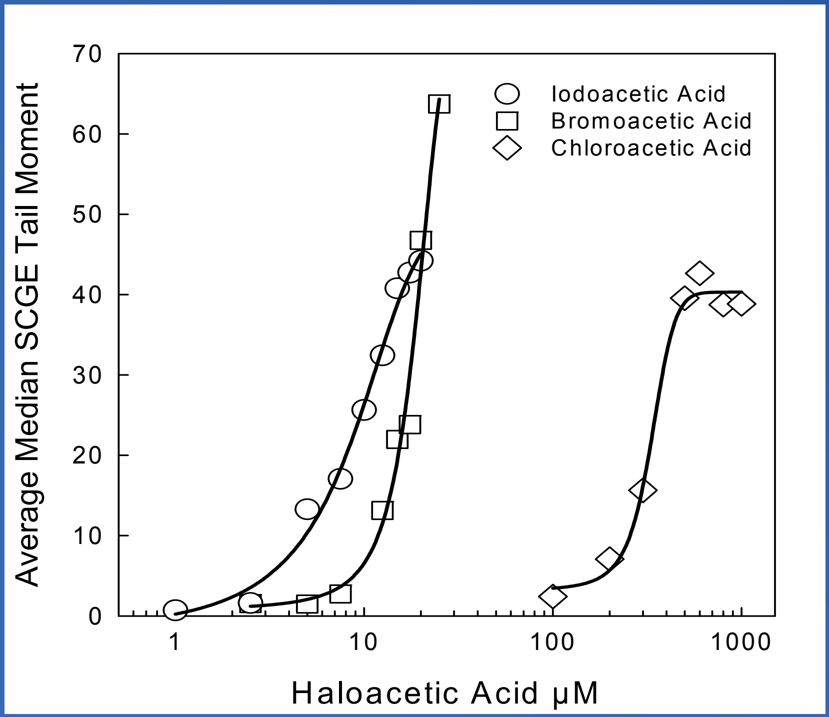


CHO Cells

Plewa et al., ES&T. 2004, *38*, (18), 4713-4722.

Slide courtesy of Michael Plewa, Univ. IL

New Human Cell Results



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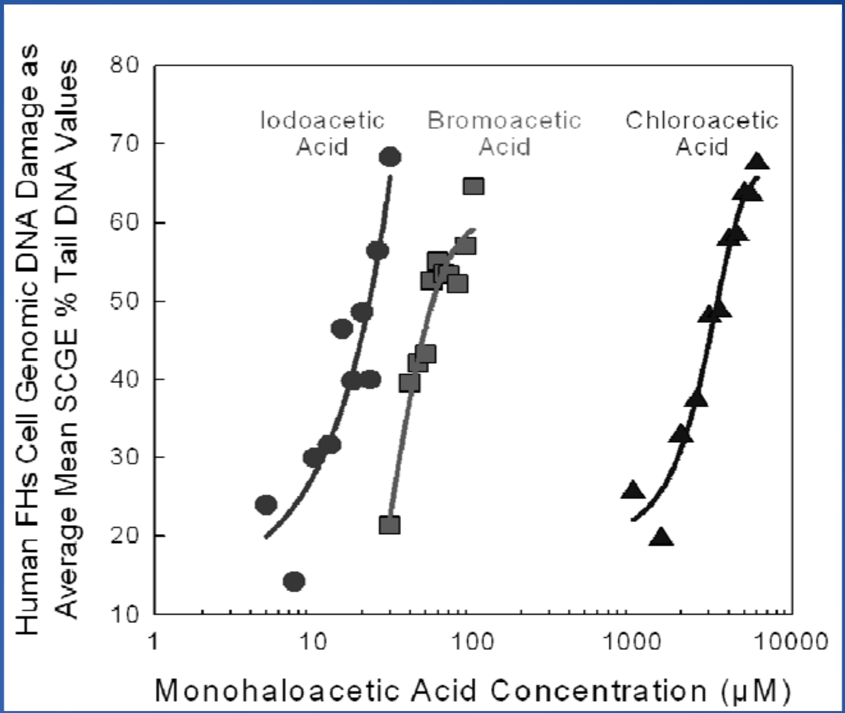


Human Cells

Attene-Ramos, Wagner, Plewa, *ES&T, 2010, 44 (19), 7206-7212*.

Nontransformed human small intestine epithelial cells

waterCAMPwS

Slide courtesy of Michael Plewa, Univ. IL

Four Lab Study

Integrated Disinfection By-products Mixtures Research: Toxicological and Chemical Evaluation of Alternative Disinfection Treatment Scenarios

A collaborative effort between:

NHEERL (National Health and Environmental Effects Research Laboratory), RTP

NERL (National Exposure Research Laboratory), Athens

NRMRL (National Risk Management Research Laboratory), Cincinnati

NCEA (National Center for Environmental Assessment), Cincinnati

Purpose:

To address concerns related to potential health effects from exposure to DBPs that cannot be addressed directly from toxicological studies of individual DBPs or simple DBP mixtures

1st phase: Published in *J. Toxicol. Environ. Health 2008* (series of 7 papers)

2nd phase: Published in *Environ. Sci. Technol.* 2010 (Chemistry paper)

Planning follow-up 4-Lab Chloramination Study

Four Lab Study: Linking DBPs measured to overall toxicity effects

In vitro:

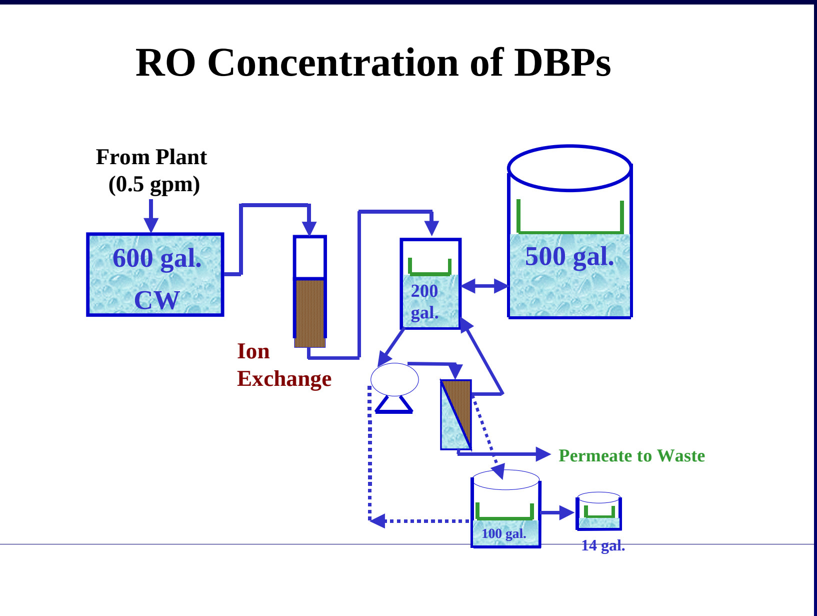
- Reproductive/developmental
- Mutagenicity
- Carcinogenicity
- Neurotoxicity
- Metabolism

In vivo:

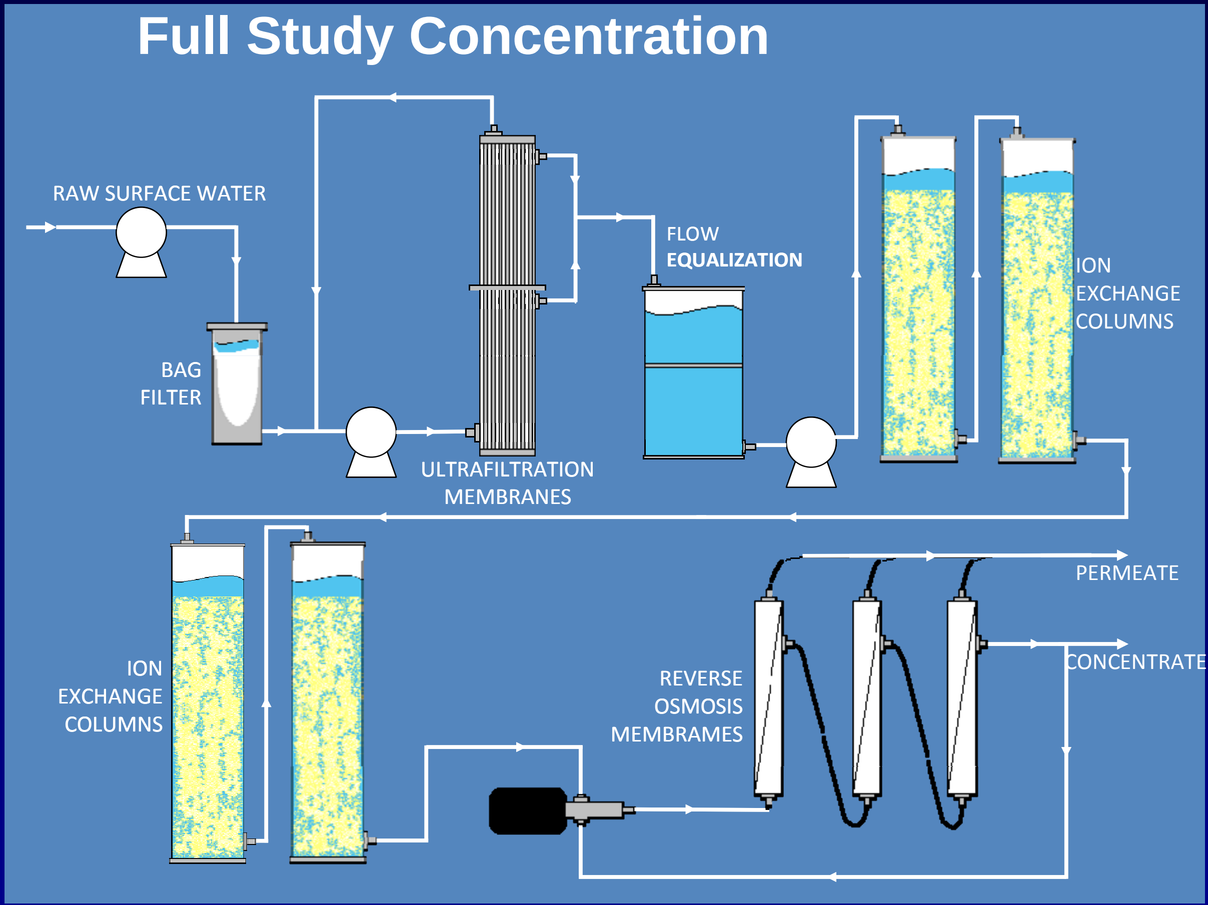
- Reproductive/developmental
- Mutagenicity/carcinogenicity
- Immunotoxicity
- Hepatic/renal toxicity
- Neurotoxicity/developmental neurotoxicity
- Kinetics/metabolism

Chemistry: 70 Priority DBPs quantified and >100 DBPs comprehensively identified using GC/MS

Jane Ellen Simmons



1st Phase:
Cl_2 & O_3-Cl_2; treated water first
Concentrated after



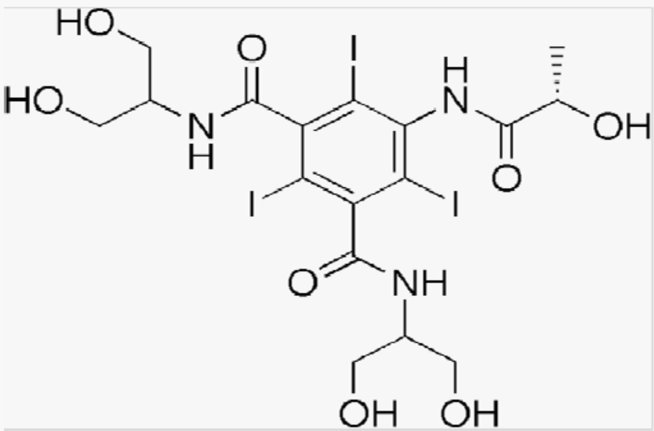
2nd Phase:
Concentrated NOM first
Treated with Cl_2 after

Rats can't drink organic solvents!

DBPs can also form from pollutants…

- Pharmaceuticals
- Pesticides
- Antibacterial agents
- Estrogens
- Textile dyes
- Bisphenol A
- Parabens
- Alkylphenol ethoxylate surfactants
- Algal toxins

Formation of iodo-DBPs from X-ray contrast media



Iopamidol

+ NOM $\xrightarrow[NH_2Cl]{HOCl}$ Iodo-DBPs

Duirk, Lindell, Cornelison, Kormos, Ternes, Attene-Ramos, Osiol, Wagner, Plewa, and Richardson, *ES&T* 2011, 45, 6845-6854.

Iodo-DBP Occurrence Study

	Iodide (μg/L)	Sum iodo-acids (μg/L)	Sum iodo-THMs (μg/L)
Plant 2	1.0	0.37	4.9
Plant 4	ND	0.10	1.2
Plant 11	1.5	0.21	2.3
Plant 15	ND	0.17	2.4

Detection limit = 0.13 μg/L

Richardson et al., *Environ. Sci. Technol.* 2008, 42, 8330-8338.

ICM in U.S. Drinking Water Sources (ng/L)

	Iopamidol	Iomeprol	Iopromide	Iohexol	Diatrizoate
Plant 1	11	ND	ND	ND	ND
Plant 2	510	ND	24	120	93
Plant 4	110	ND	6	49	ND
Plant 10	ND	ND	ND	ND	ND
Plant 11	100	ND	ND	85	ND
Plant 12	280	ND	ND	120	ND
Plant 13	ND	ND	ND	ND	ND
Plant 15	2700	ND	25	ND	ND
Plant 17	ND	ND	ND	ND	ND
Plant 19	ND	ND	ND	ND	ND

Courtesy of Thomas Ternes, Federal Institute of Hydrology, Germany

ICM measured using LC/ESI-MS/MS; DLs = 5-20 ng/L

ICM in U.S. Drinking Water Sources (ng/L)

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Controlled Laboratory Reactions

Experiments

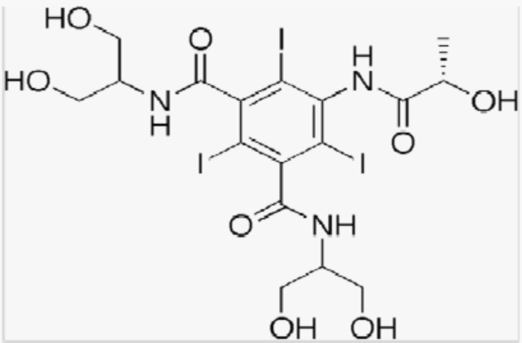
- React ICM with HOCl, NH_2Cl (with and without NOM)
- 3 pHs
- Follow formation of iodo-DBPs
- Identify reaction products and intermediates
- Measure genotoxicity

Methods

- Iodo-THMs: GC/EI-MS
- Iodo-Acids: GC/NCI-MS (with derivatization)
- Iopamidol (and other ICM): LC, LC/MS/MS
- Larger MW products and intermediates: LC/MS/MS
- Genotoxicity: Chinese hamster ovary cells, single cell gel electrophoresis

Cristal and Steve

Results

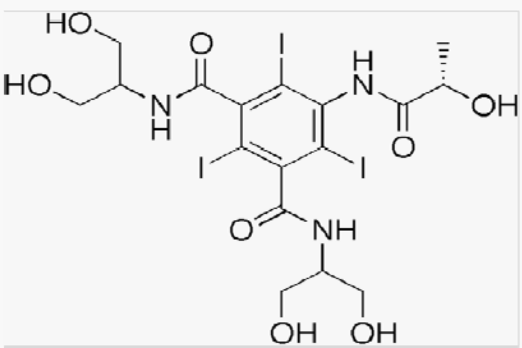


Iopamidol

HOCl → NH_2Cl

Iodo-DBPs

trace



Iopamidol

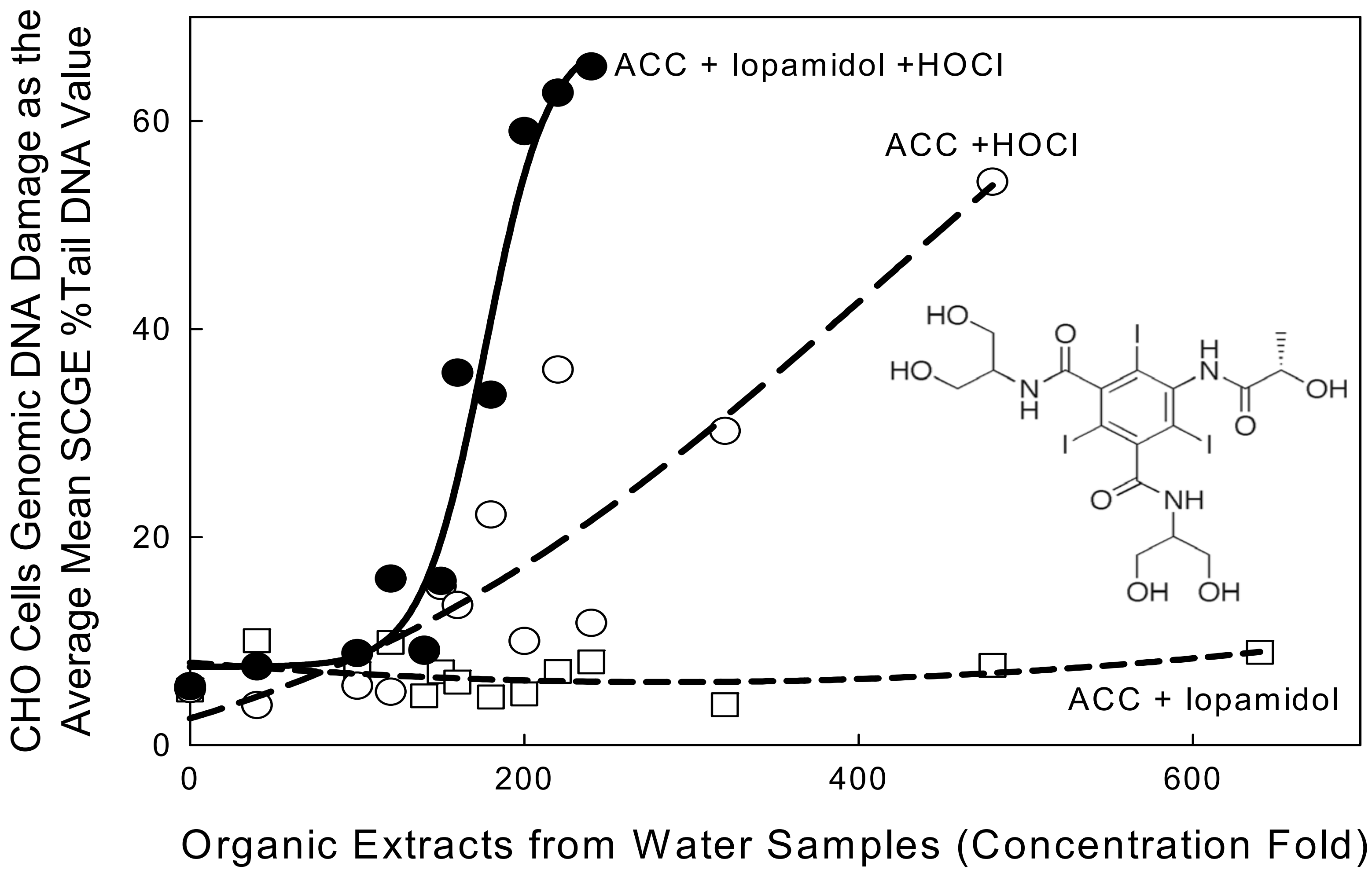
+ NOM

HOCl → NH_2Cl

Iodo-DBPs ✓

Iodo-THMs
&
Iodo-Acids

Genotoxicity of Chlorinated Waters Containing Iopamidol



In closing….

Ever wonder what happens when you have to scale things up for toxicity testing???

The Land of Extraordinarily Large Lab Equipment

Chris

Toxicity?
20 L → 1 mL

Steve

Cristal

Acknowledgments

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Thomas Ternes

Michael Plewa

Jim Lazorchak

Tammy Jones-Lep

Jorge Gardea-Torresdey