Modeling of DOC and Disinfection By-Product Precursors in the NYC Water Supply

Catskill Environmental Research & Monitoring Conference

October 28, 2016

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Cristiano

as in…….

Cristiano Ronaldo

Portuguese soccer player

World Player of the Year:
2008, 2013, 2014

Commonly appears on
Top 10 lists of
"Best Looking Men"

Perfect!

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Modeling of DOC and Disinfection By-Product Precursors in the NYC Water Supply

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Outline

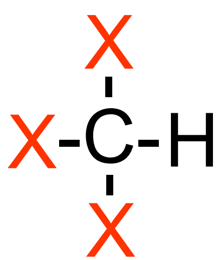
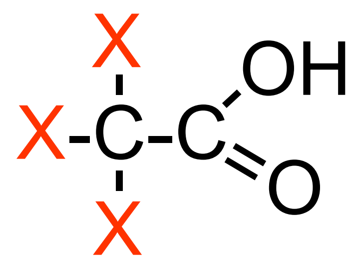
- Organic carbon (OC), disinfection byproducts (DBPs), and DBP precursors
- Sources, fate, and transport of OC and precursors
- Modeling approaches for OC and precursors
- DBP precursor mass balance modeling
- Summary

What are Disinfection By-Products?

Halogenated organic compounds formed when certain organic compounds in source water (precursors) are chlorinated.

Two classes of DBPs are suspected human carcinogens, and are regulated by the federal Safe Drinking Water Act:

X is Cl or Br

trihalomethanes (THMs)	haloacetic acids (HAAs)
 trihalomethane if X is Cl - chloroform	 trihaloacetic acid – type of HAA if X is Cl - trichloroacetic acid
Total trihalomethane TTHM = sum of 4; Limit = 80 µg/liter	Total haloacetic acid HAA5 = sum of 5 HAAs; Limit = 60 µg/liter

Organic Carbon in Streams, Reservoirs

THM precursors (THMP) - the subset of DOC that, when chlorinated, produce THMs

HAA precursors (HAAP) - the subset of DOC that, when chlorinated, produce HAAs

A subset of POC can also produce THMs, HAAs; found to be small when measured

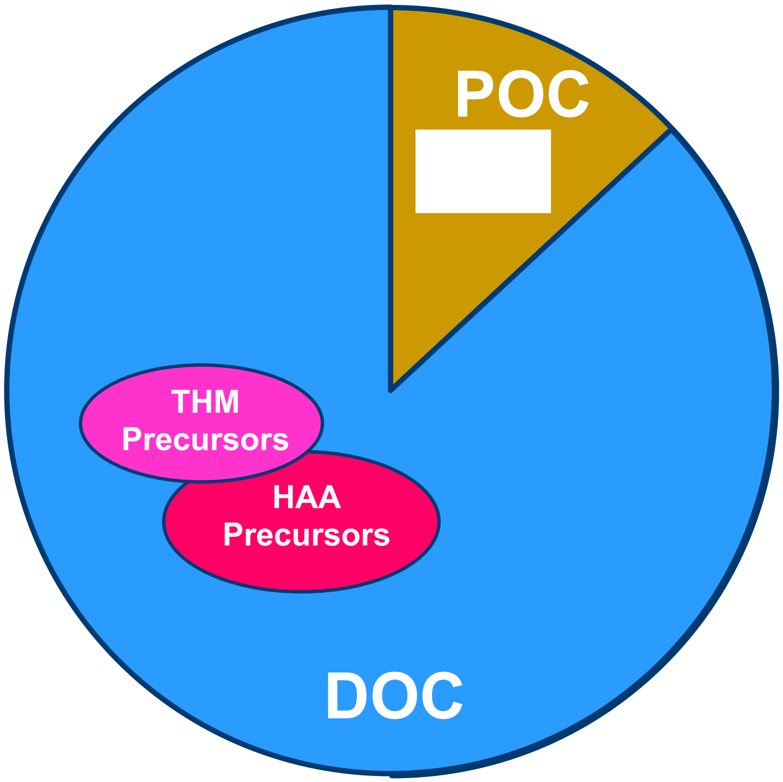
For simplicity here, neglect THM, HAA production from POC

Consider only regulated DBPs:

DBP precursor =
(*THM precursor* + *HAA precursor*)

(there are unregulated DBPs)

~7000 compounds



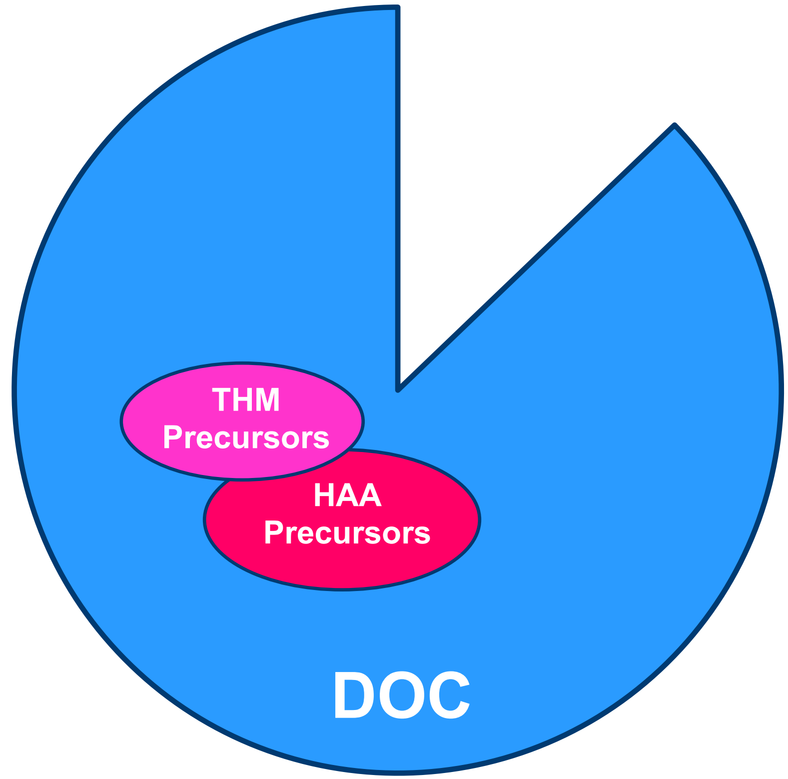
DOC – dissolved organic carbon
POC – particulate organic carbon (dead)
TOC – total organic carbon = (DOC + POC)

Organic Carbon in Streams, Reservoirs

$$\left[\frac{\text{no. of precursor compounds}}{\text{no. of DOC compounds}}\right]$$

(~7000)

This ratio is relatively constant – a compound either reacts with chlorine, or not



$$\left[\frac{\text{mass or concentration of precursors}}{\text{mass or concentration of DOC}}\right]$$

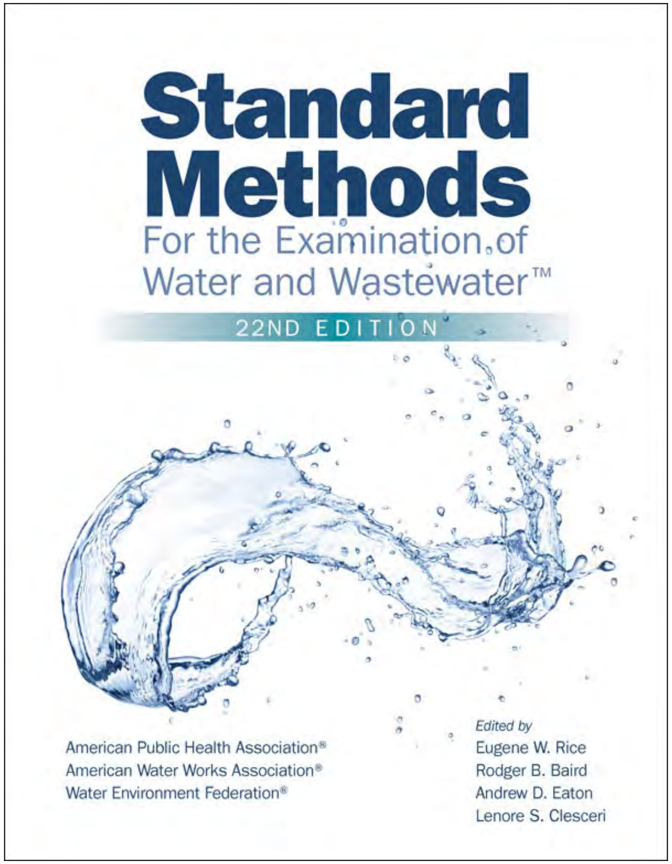
This ratio is variable:

- *over time at a stream or reservoir site*
- *from site to site*

DBP Formation Potential (DBPFP)

- “Precursor” is a general, qualitative term
- Formation Potential test quantifies THM, HAA precursor concentrations

- The standard laboratory test for quantifying THM and HAA precursor concentrations
- Chlorine dosage – high enough so that THM, HAA formation not limited by dosage (significantly higher than used by NYC)
- Water temperature = 25 ^{o}C, pH=7.0
- Incubate for 7 days (detention time)
- Using Gas Chromatograph measure:
  - 4 THMs; THM Formation Potential (THMFP)
  - 5 HAAs; HAA Formation Potential (HAAFP)

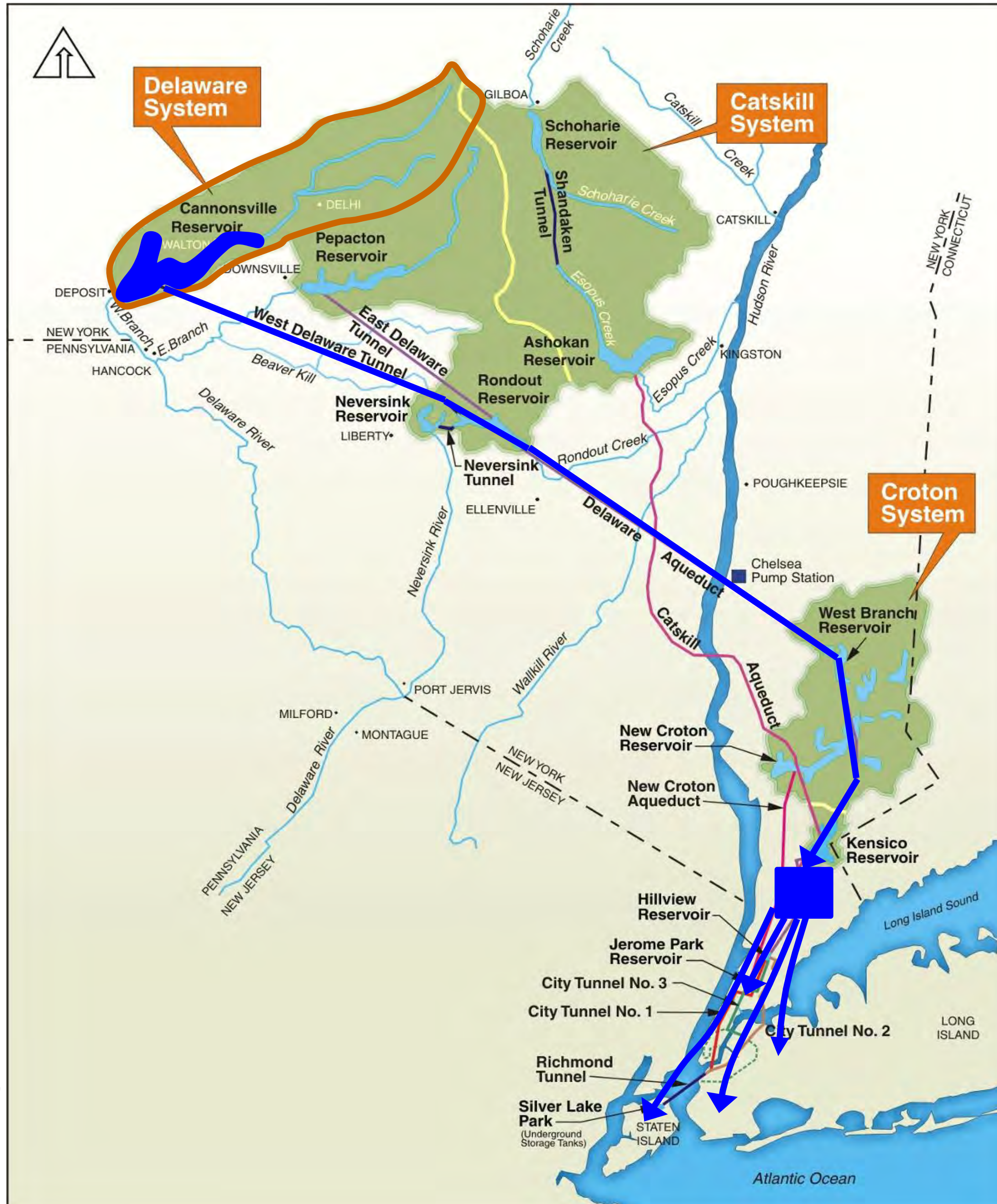


Organic Carbon, Precursors, DBPs

- Watershed sources of organic carbon (OC) and precursors:
  - Plant litter, wetlands
  - Anthropogenic: wastewater, urban stormwater, agriculture
  - OC and precursors undergo decomposition during transport to reservoir
- In reservoirs:
  - OC and precursor production associated with algal production and decay
  - mix of watershed and reservoir OC and precursors experience: hydrolysis, biodegradation, photolysis

Organic Carbon, Precursors, DBPs

- Chlorine added to inactivate pathogens; formation of disinfection by-products begins here; UV disinfection also
- Finished (disinfected) drinking water distributed to customers; DBP concentration at tap depends on
  - Water temperature, pH
  - Chlorine dose
  - Contact time from chlorination to tap
- DBP (tap) < DBPFP (supply)
- Regulations apply at tap



Role of Models

- ***Long-term planning:*** evaluate impacts of:
  - DEP's watershed management programs, land use
  - climate change and extreme events
- Watershed model: predict impacts on loading of carbon, precursors, and nutrients to reservoirs
- Reservoir model: predict impacts on precursors in the water supplied to NYC; relative roles of watershed and reservoir sources of precursors

DEP's Operations Support Tool

NYC Environmental Protection

- NYC system: 19 reservoirs, 3 controlled lakes, three major reservoir systems (Catskill, Delaware unfiltered; Croton filtered) each served by a major aqueduct - in general, significant flexibility in meeting water demand
- Weather events cause degraded water quality that is:
  - Commonly episodic, lasting a few days or weeks
  - Rarely system-wide; wise, selective use of sources (reservoirs), and selective withdrawal during an episode improves quality of the water supply
- Operations Support Tool (OST) – a software application with associated in-situ sensors, databases, WQ model, etc.
- Guides short-term (days, weeks) system operation given:
  - System characteristics, capacities
  - Current conditions (storage, water quality, outages)
  - Forecasts of future weather, streamflow
  - Operational requirements, constraints, rules, priorities

Role of Models

NYC Environmental Protection

- ***Operations***: incorporate reservoir DBP precursor model into the Operations Support Tool (OST); include minimizing precursors and compliance with DBP regulations, together with other factors, in operations

- Both DOC and DBPFP are laboratory tests

- Related challenge: develop in-situ proxy (optical) sensors for near-real time measurement of DOC and DBPFP
(not discussed here)

Modeling Approaches

DEP is pursuing two alternative modeling approaches for predicting THM, HAA precursors in reservoirs:

❖ ***Approach 1:*** Develop mechanistic (mass balance) model for organic carbon; predict THMFP, HAAFP empirically from DOC

- Organic carbon model – we are applying and testing the General Lake Model/Aquatic Ecodynamics (GLM / AED), a widely-used open-source organic carbon model

❖ ***Approach 2:*** Develop mechanistic (mass balance) model for THM and HAA precursors

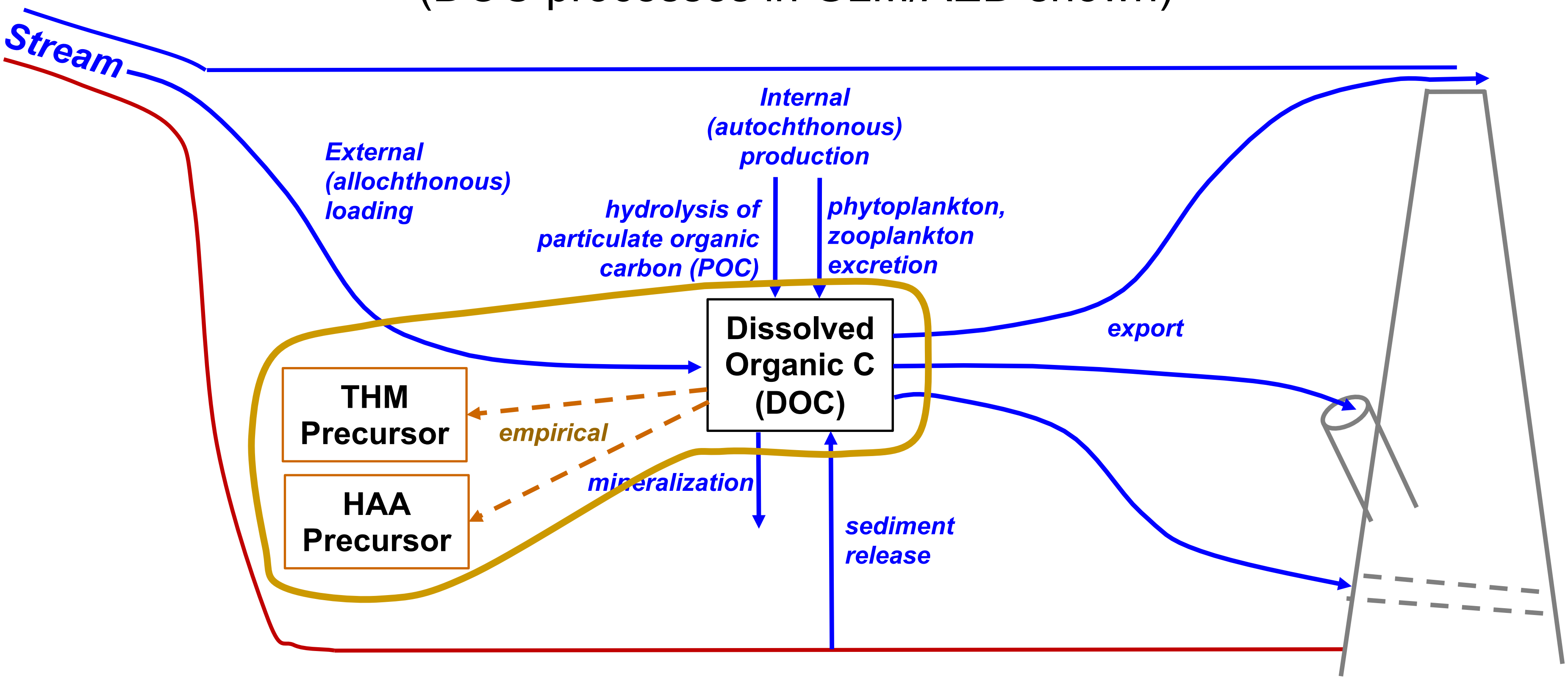
- Consider and quantify stream loading, export, and individual internal production and loss processes for THM and HAA precursors

Initial model testing for Cannonsville and Neversink

Modeling Approach #1

DBP precursor model based on DOC model

(DOC processes in GLM/AED shown)



- Start with mass balance model for various forms of organic carbon: DOC, POC, Algal C, Zooplankton C (a carbon-based nutrient-phytoplankton model)
- <u>No mass balance for precursors</u>

  utilize empirical relationships for DOC $\longrightarrow$ precursors. For example:

  THMFP (μg/l) = 43.8 (DOC mg/l)$^{1.25}$ (Chapra et al., 1997, J. Environ. Engr.)

Data

- Best available stream and reservoir monitoring program for DOC and Formation Potential collected in 1998
- THMFP Only (No HAAFP)
- Tributary THMFP, DOC sampling:
  - Weekly sample near inflow of W. Branch Delaware R. (major Cannonsville tributary)
  - Weekly sample near inflow of Neversink R. (major Neversink tributary)
  - Limited storm event sampling
- Reservoir water column THMFP, DOC sampling:
  - Weekly profile at Cannonsville Site 4, 3-meter depth interval
  - Biweekly profile at Neversink Site 1, 3-meter depth interval

DOC – THMFP Regression

Cannonsville and Neversink:
June 3 to November 29, 1998

$$\boldsymbol{THMFP = 99.8\ DOC^{0.369}}$$

DOC – THMFP Regression Summary

Cannonsville:

	a	*b*	RMSE	*n*	r^2
Epilimnion	174	-0.086	59	63	0.01
Hypolimnion	105	0.069	38	81	0.01
All water column	115	0.149	54	144	0.02
Tributaries	112	0.362	60	46	0.14
Water Col and Tribs	114	0.195	57	190	0.04

Neversink:

	a	*b*	RMSE	*n*	r^2
Epilimnion	120	0.240	35	25	0.04
Hypolimnion	97.3	0.502	25	50	0.29
All water column	99.8	0.483	36	75	0.26
Tributaries	91.7	0.883	32	10	0.87
Water Col and Tribs	90.1	0.683	38	85	0.58

	a	*b*	RMSE	*n*	r^2
All Data	99.8	0.369	53	275	0.18

RMSE- root mean square error (μg-THMFP/liter)

$$THMFP = a\ DOC^{b}$$

THMFP (μg/liter), DOC (mg/liter)

Compare RMSE to regulatory limit of 80 μg/liter – *we would like to do better!*

Conclusion:

All DOC is not the same in terms of THM yield; model needs to consider that diversity

Modeling Approach #1

How to increase accuracy of empirical models?

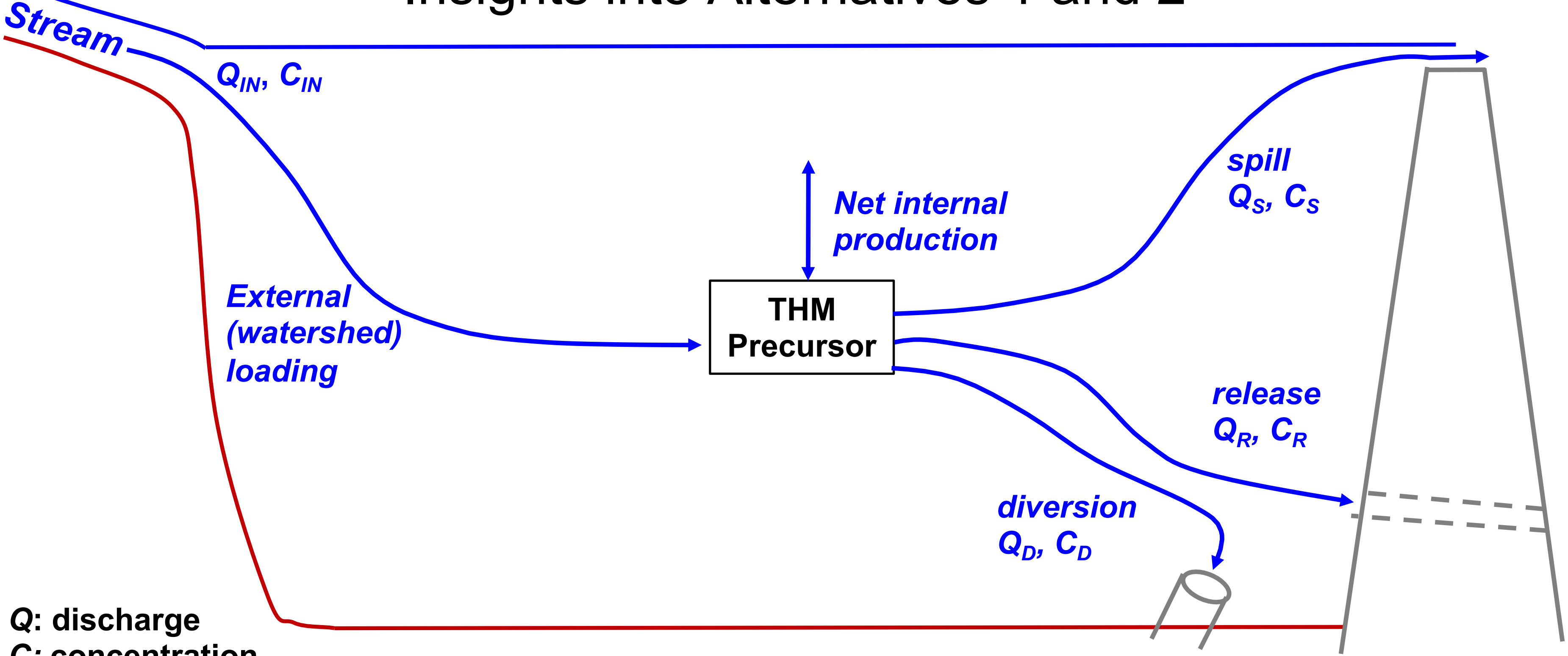
Studies attribute variability in DOC – DBPFP relationship to diversity of the myriad compounds that make up DOC

Potential Solution: explicitly include 2 or more DOC “pools” in the model. Some alternatives:

- Allochthonous and autochthonous DOC
- Labile and refractory DOC
- Perhaps further division of these pools

THMFP, DOC Reservoir Mass Balance

Insights into Alternatives 1 and 2



change in reservoir mass / time interval

$$\frac{\Delta M}{\Delta t} = \underbrace{Q_{IN}C_{IN}}_{\text{external loading}} - \underbrace{\underbrace{Q_S C_S}_{\text{spill}} - \underbrace{Q_R C_R}_{\text{release}} - \underbrace{Q_D C_D}_{\text{diversion}}}_{\text{export}} + P$$

Net Internal Production:

= Σ (production processes) - Σ (loss processes)

Water Balance

Over the period June 3 to November 29, 1998

Cannonsville:

	Water Vol (BG)
Δ Volume	-68.7
Total Inflow	51.3
Total Outflow	120
Net Internal	0

Neversink:

	Water Vol (BG)
Δ Volume	- 20.6
Total Inflow	16.7
Total Outflow	37.3
Net Internal	0

- Outflow exceeds inflow
- Both reservoirs experienced ~17 m drawdown during this period

BG- billion gallons; MT – metric tons

THMFP and DOC Mass Balance

Over the period June 3 to November 29, 1998

Cannonsville:

	Water Vol (BG)	THMFP (MT)
Δ Volume/Mass	-68.7	- 48.0
External Load	51.3	41.6
Export	120	66.6
Net Internal	0	- 23.0

From measured inflow, outflow, storage, concentrations

$= -48.0 - 41.6 + 66.6$

Neversink:

	Water Vol (BG)	THMFP (MT)
Δ Volume/Mass	- 20.6	- 14.8
External Load	16.7	17.6
Export	37.3	21.2
Net Internal	0	- 11.1

From measured inflow, outflow, storage, concentrations

$= -14.8 - 17.6 + 21.2$

BG- billion gallons; MT – metric tons

THMFP and DOC Mass Balance

NYC Environmental Protection

Over the period June 3 to November 29, 1998

Cannonsville:

	Water Vol (BG)	THMFP (MT)	DOC (MT)
Δ Volume/Mass	-68.7	- 48.0	-1400
External Load	51.3	41.6	270
Export	120	66.6	1020
Net Internal	0	- 23.0	- 650

- THMFP and DOC are non-conservative
- Net internal production/loss same order of magnitude as other terms

Neversink:

	Water Vol (BG)	THMFP (MT)	DOC (MT)
Δ Volume/Mass	- 20.6	- 14.8	- 183
External Load	16.7	17.6	127
Export	37.3	21.2	234
Net Internal	0	- 11.1	- 76

- Net internal production/loss of THMFP and DOC in both reservoirs is negative
- The net effect of in-reservoir processes is the loss of both THMFP and DOC

BG- billion gallons; MT – metric tons

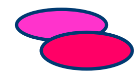
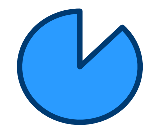
Reservoir Comparison

Convert net internal production to volumetric rate (divide by reservoir volume)

Net Internal Production (mg/m^3/day) :

	THMFP	DOC
Cannonsville	-0.171	-10.6
Neversink	-0.530	-6.90

- DOC larger at Cannonsville; but THMFP larger at Neversink
- Reservoir processes did not act proportionally on

 and 

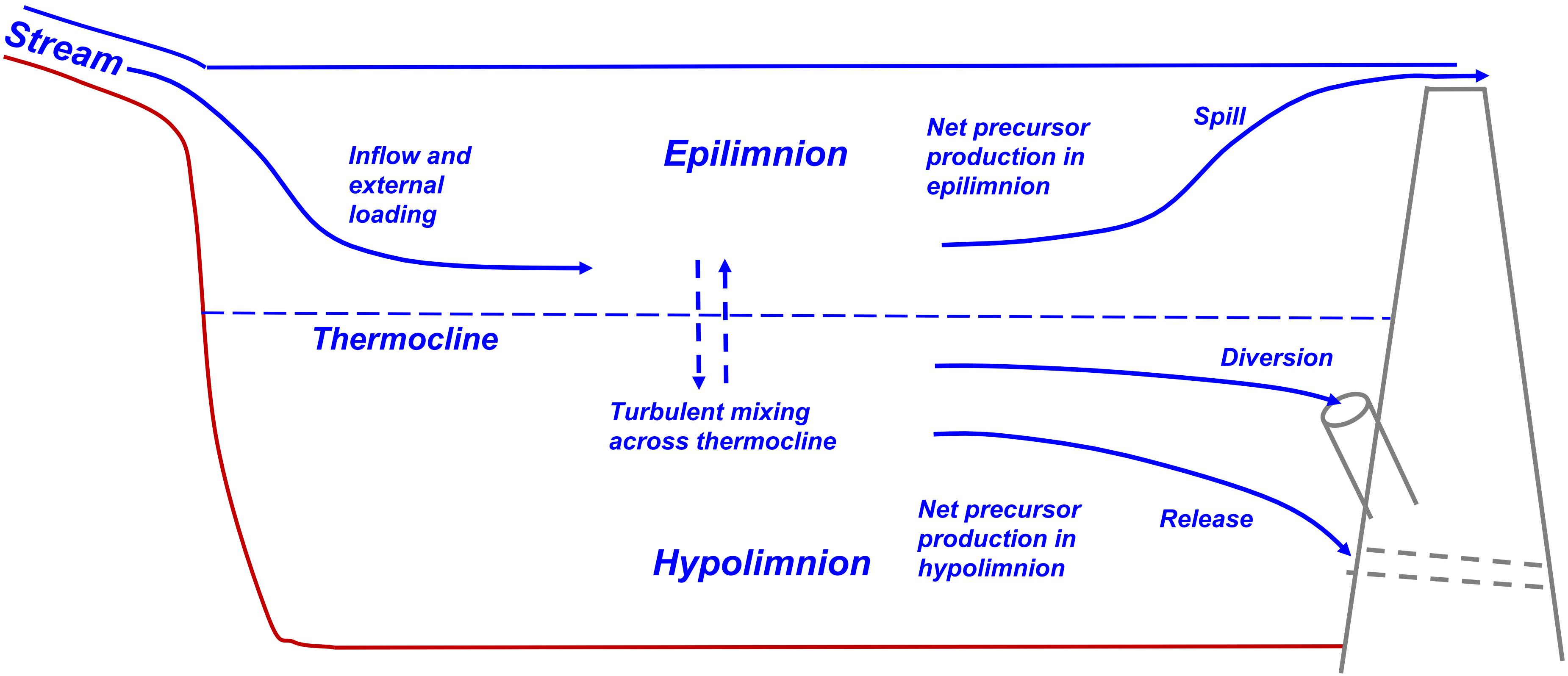
Convert external (watershed) load to areal rate (divide by watershed area)

External Load (kg/km^2/day) :

	THMFP	DOC
Cannonsville	0.212	1.375
Neversink	0.448	3.246

- Neversink has roughly double the areal loading rates of both THMFP and DOC

THMFP, DOC Two Layer Mass Balance



- Turbulent mixing coefficient at thermocline – determined from rate of heating of hypolimnion
- Similar mass balance analysis used to determine net production in each layer

Net Internal Production of THMFP, DOC

Cannonsville:

	THMFP (MT)	THMFP (mg/m³/d)	DOC (MT)	DOC (mg/m³/d)	
Epilimnion	5.4	0.30	180	9.9	production > loss
Hypolimnion	-14	-0.47	-740	- 27	loss > production

- Cannonsville (eutrophic in 1998) has net production in upper waters, net depletion in lower waters external load

Neversink:

	THMFP (MT)	THMFP (mg/m³/d)	DOC (MT)	DOC (mg/m³/d)	
Epilimnion	-4.3	-0.61	-17	-2.4	loss > production
Hypolimnion	-6.8	-0.64	-58	-5.4	loss >> production

- Neversink (oligotrophic then and now) has net depletion in both layers

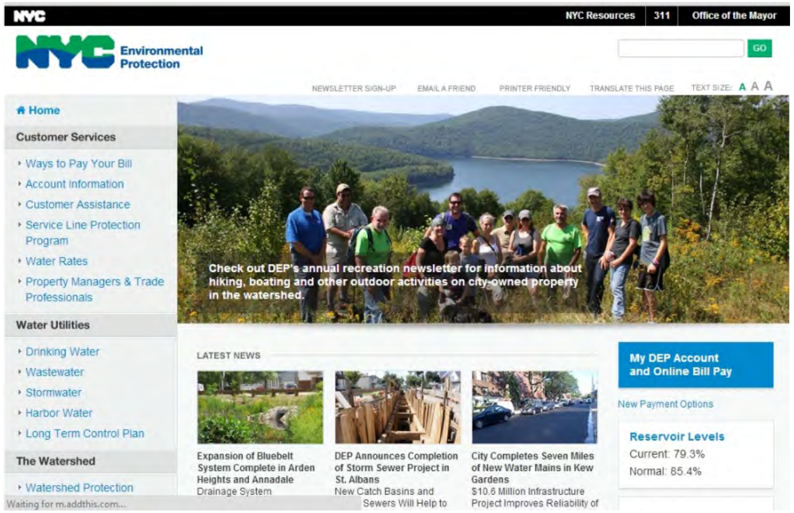
Model needs to consider vertical variation in water quality;
a completely-mixed reservoir model is not adequate

MT – metric tons

Summary

- Modeling Alternative #1: regression models to predict precursor concentration from DOC have large errors; likely associated with variability in the mix of compounds that make up DOC
- Variability, errors can be reduced by use of 2 or more pools of DOC.
- Modeling Alternative #2: a mass balance analysis for THM precursors and DOC was conducted for Cannonsville and Neversink Reservoirs, using 1998 observations.
- Calculations showed that net internal (autochthonous) THM precursor production was
  - Of same order of magnitude as external loading (allochthonous)
  - For both reservoirs, net production was negative; net effect of reservoir processes was loss of both precursors and DOC
  - Net production of THM precursor and DOC was larger in epilimnion than hypolimnion; in surface waters of Cannonsville, net production was positive
- We are progressing on both modeling alternatives, leading to comparison, selection, and perhaps integration of the two alternatives

For more information…



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Questions?