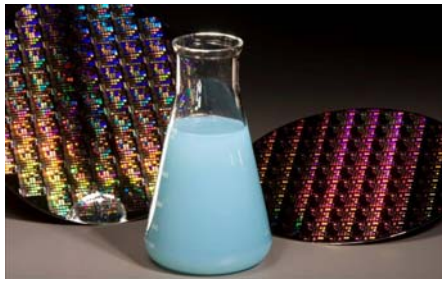
EHS Assessment of Chelators and Biocides Utilized in Semiconductor Manufacturing

Reyes Sierra

Department of Chemical and Environmental Engineering
The University of Arizona
E-mail: rsierra@email.arizona.edu

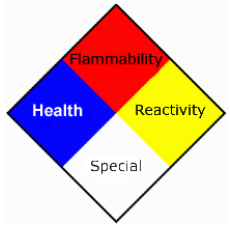
Objectives

I) Review trends in the use of biocides and chelators in wet cleans & CMP.



II) Literature review:

- EHS characteristics of main biocides and chelators

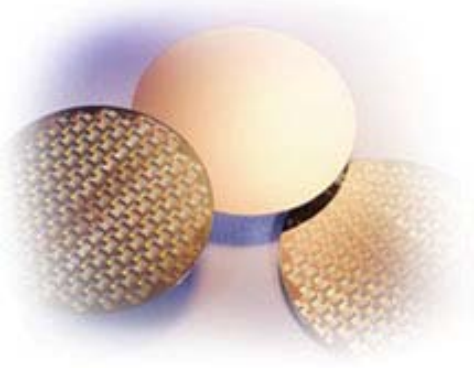


- Impact on:
  - Biological wastewater treatment processes.
  - Species used in effluent ecotoxicology monitoring.

Method of Approach

- Inventory of biocides and chelators in wet cleans and CMP:

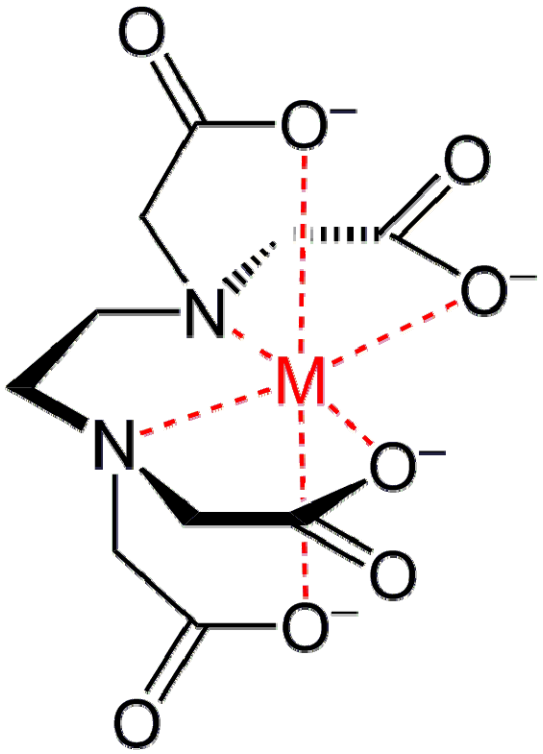
  Consultation with industry, suppliers, experts



- EHS assessment / fate in biological treatment systems:

  Review of literature and public databases

Chelators



Chemical structure of EDTA-metal chelate.

Chelators in Semiconductor Manufacturing

CMP

- Used to complex Cu ions.

Back-end-of-line cleaning

- Used for stripping photoresists, and
- Removing organic/inorganic residues from substrates subjected to gas phase etching, post-etching and CMP.

Front-end-of-line cleaning

- Generally do not utilize chelators

Survey of Chelator Use by ISMI Member Companies

Organic chelators listed in the survey conducted by ISMI among member companies:

- EDTA
- DTPA
- HEDTA
- NTA

Aminopolycarboxylates

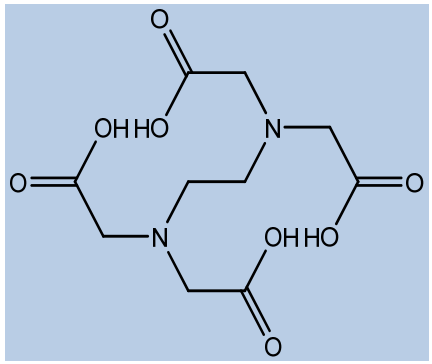
- Citric acid
- Maleic acid
- Malonic acid

Polycarboxylates

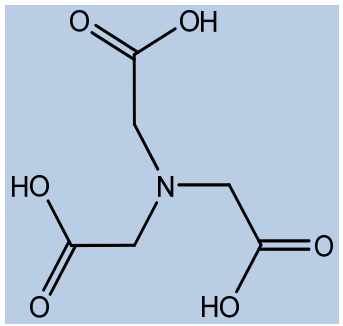
Chelators in Semiconductor Manufacturing

- Amino-polycarboxylates (eg. EDTA, active components in Versene / Trilon®)
- Polycarboxylates (eg. citric acid) & simple organic acids (eg. lactate)
- Amino acids and derivatives (eg. glycine)
- Organic amines (eg. ethylenediamine)
- (Phosphonates)

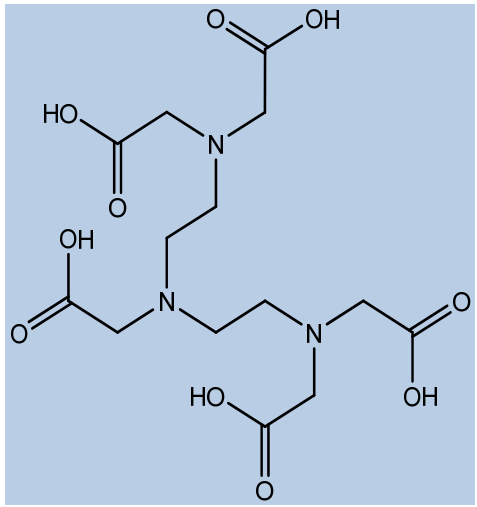
Aminopolycarboxylate chelators



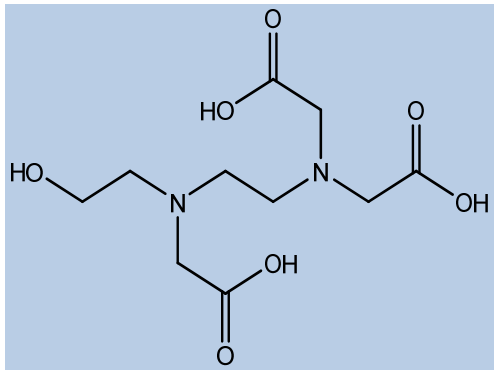
EDTA



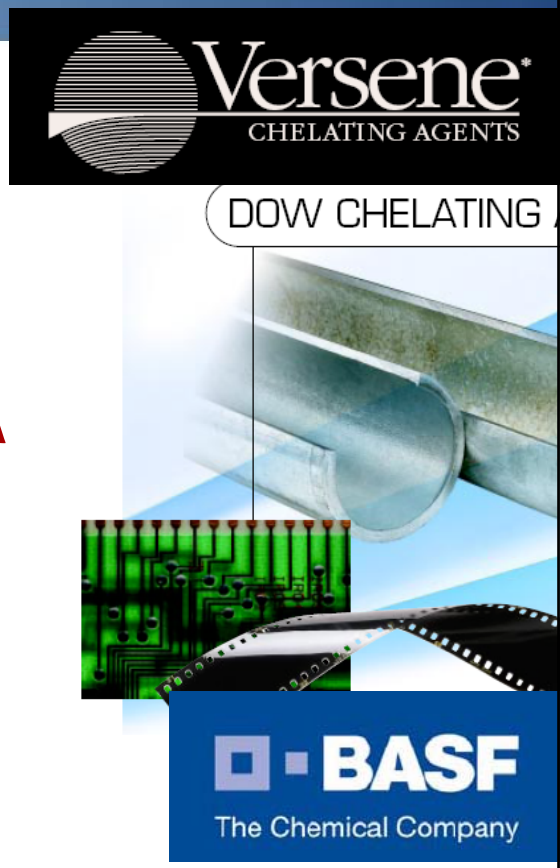
NTA



DPTA



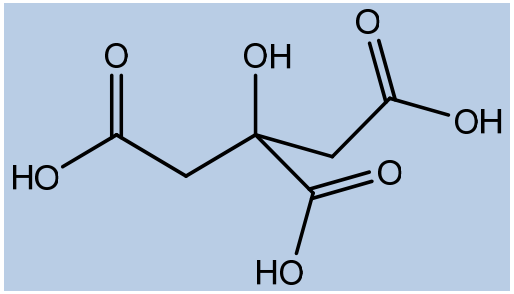
HEDTA



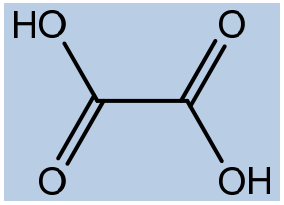
EDTA (Ethylene-diaminetetraacetic acid);
DTPA (Diethylenetriaminepentaacetic acid);
NTA (Nitrilotriacetic acid)
HEDTA (N-(hydroxyethyl)-ethylenediaminetriacetic acid)

Other chelators: Polycarboxylates, Glycine derivatives

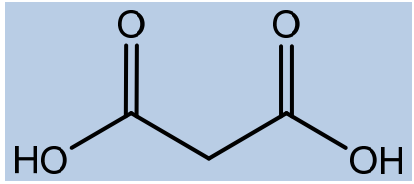
Polycarboxalate chelators



Citric acid

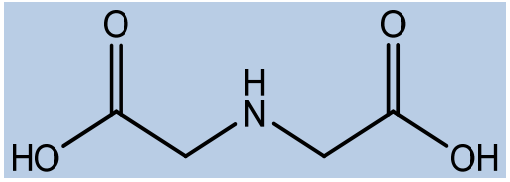


Oxalic acid

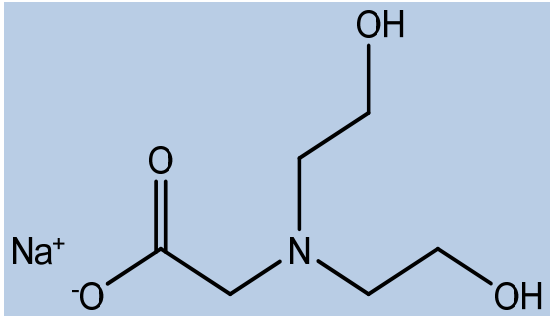


Malonic acid

Glycine-based chelators



Glycine
(iminodiacetic acid)



Dihydroxyethylglycine

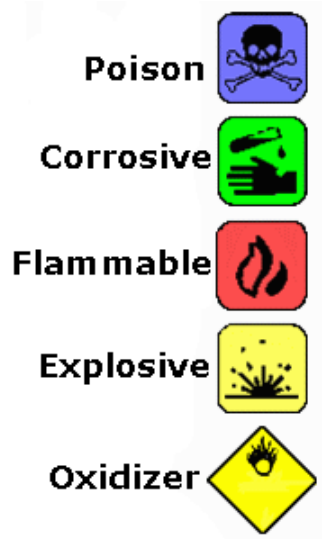
Chelators: ESH Characteristics

Compounds are solid at room temperature, low vapor pressure

Exposure: Potential for dermal and inhalation exposure

Hazards:

Reactivity:	No
Ignitability:	No
Corrosion:	Yes
Health:	Yes



EDTA- Approved food additive

Acceptable daily intake of Calcium-disodium EDTA (WHO) = 2.5 mg/kg♦ body weight

Health hazard Acute / chronic toxicity **Oxalic acid**

NTA (possible carcinogen) / **DTPA** (suspected teratogen)

Aminopolycarboxylates in Wastewater

Aminopolycarboxylates: Pollution ranges of waste water effluents

	EDTA (µg/L)	NTA (µg/L)	DTPA (µg/L)
Effluents of municipal sewage treatment plants			
Typical pollution	10–250	1–15	1–30
High pollution	1000	200	300
Effluents of industrial sewage treatment plants			
Typical pollution	100–20,000	100–2000	50–5000
High pollution	400,000	5000	20,000

(Schmidt et al. Environ Pollut, 2004, 131, 107-124)

Chelators: Fate in POWTs

Chelators	Biodegradation	Sorption to sludge	Removal	Microbial toxicity
Aminopolycarboxylates	EDTA – Low Others- Moderate	No/Low	EDTA –Low Others- Moderate	Yes (high conc)
Polycarboxylates/ Amino acid derivatives	Yes	No	High	No

Aminopolycarboxylates chelators: Widspread environmental contaminants

- **EDTA, NTA**, and **DPTA** are among the most abundant pollutants detected in surface water in USA and Europe.

- Typical concentrations of **EDTA** in European rivers: 0-100 µg/L.

(Schmidt et al. Environ Pollut, 2004, 131, 107-124)
(Reemtsma. Environ. Sci. Technol. 2006, 40, 5451-5458)

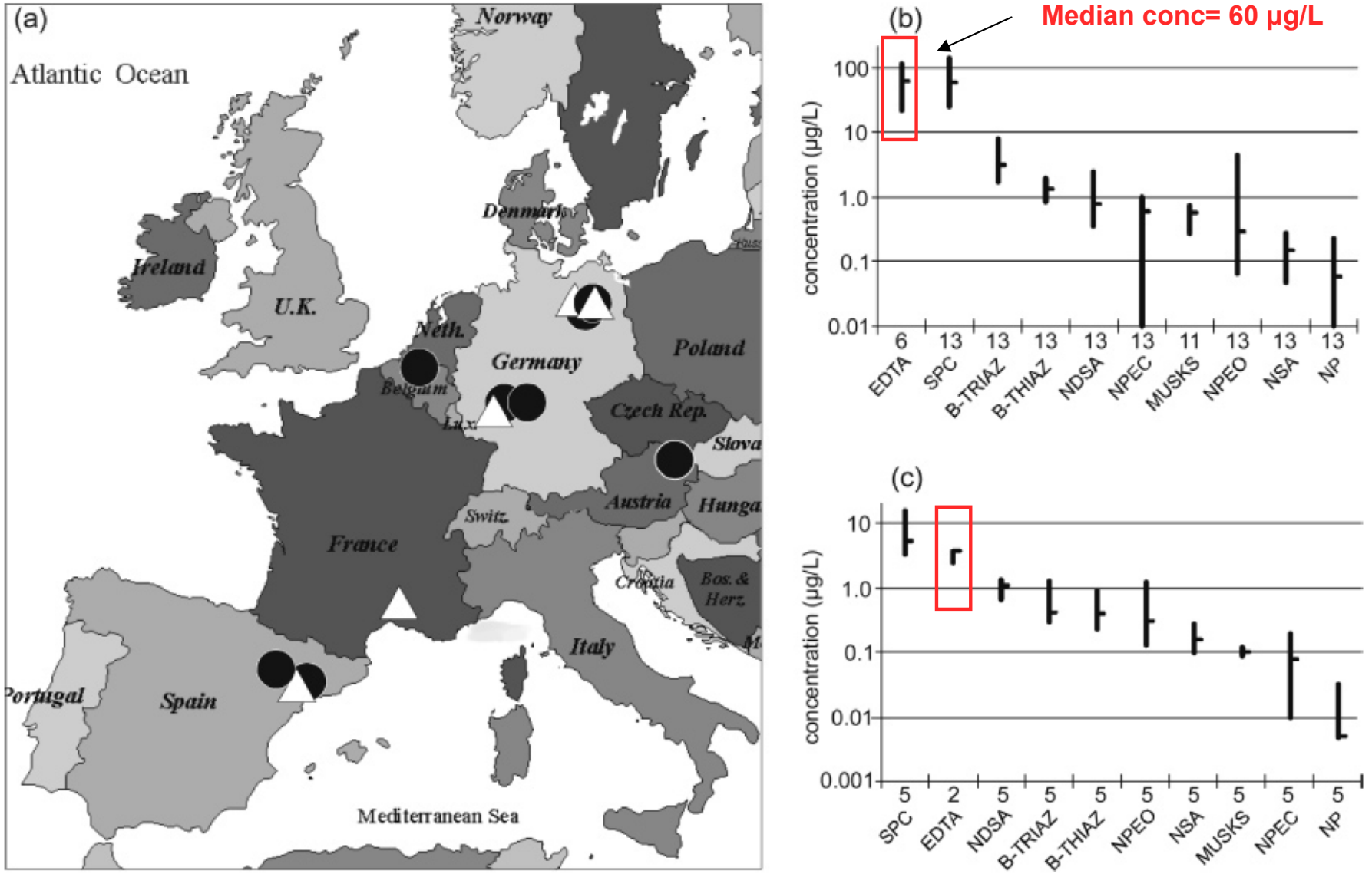


FIGURE 1. (a) Sampling locations for WWTP effluents (black dots) and surface water monitoring (white triangles). Median, 25 and 75 percentile concentrations of polar pollutant classes determined in the monitoring campaign (in μg/L) (b) of 13 effluent samples of eight WWTP in four European countries and (c) in five surface waters of different catchments in Europe. *n* denotes the numbers of samples analyzed.

Acceptable daily intake of Calcium-disodium EDTA (WHO) = 2.5 mg/kg♦ body weight.

Reemtsma. Environ. Sci. Technol. **2006**, 40, 5451-5458

Microbial and Aquatic Toxicity:
Aminopolycarboxylates

Microbial Toxicity

- No negative effects on biological treatment processes in POWTs
- Microbial toxicity could be a problem in the biological treatment of industrial wastewaters containing high chelator levels.

Aquatic Toxicity

- Moderate-low acute toxicity: LC50 ≈ hundreds of mg/L

e.g. NTA: LC50 (water fleas): 600-900 mg/L

LC50 (fathead minnows): 127 mg/L

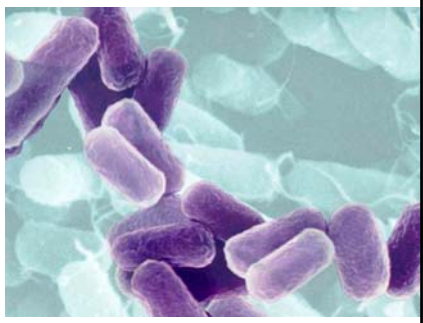
Environmental concs. of these chelators are unlikely to cause aquatic toxicity

Microbial & Aquatic Toxicity:
Aminopolycarboxylates

- No/low intrinsic toxic, toxicity due to their ability to decrease the bioavalability of essential metals.

- Toxicity depends on chelator speciation
  (pH, metal levels, hardness)

- May cause mobilization of toxic metals in the environment.

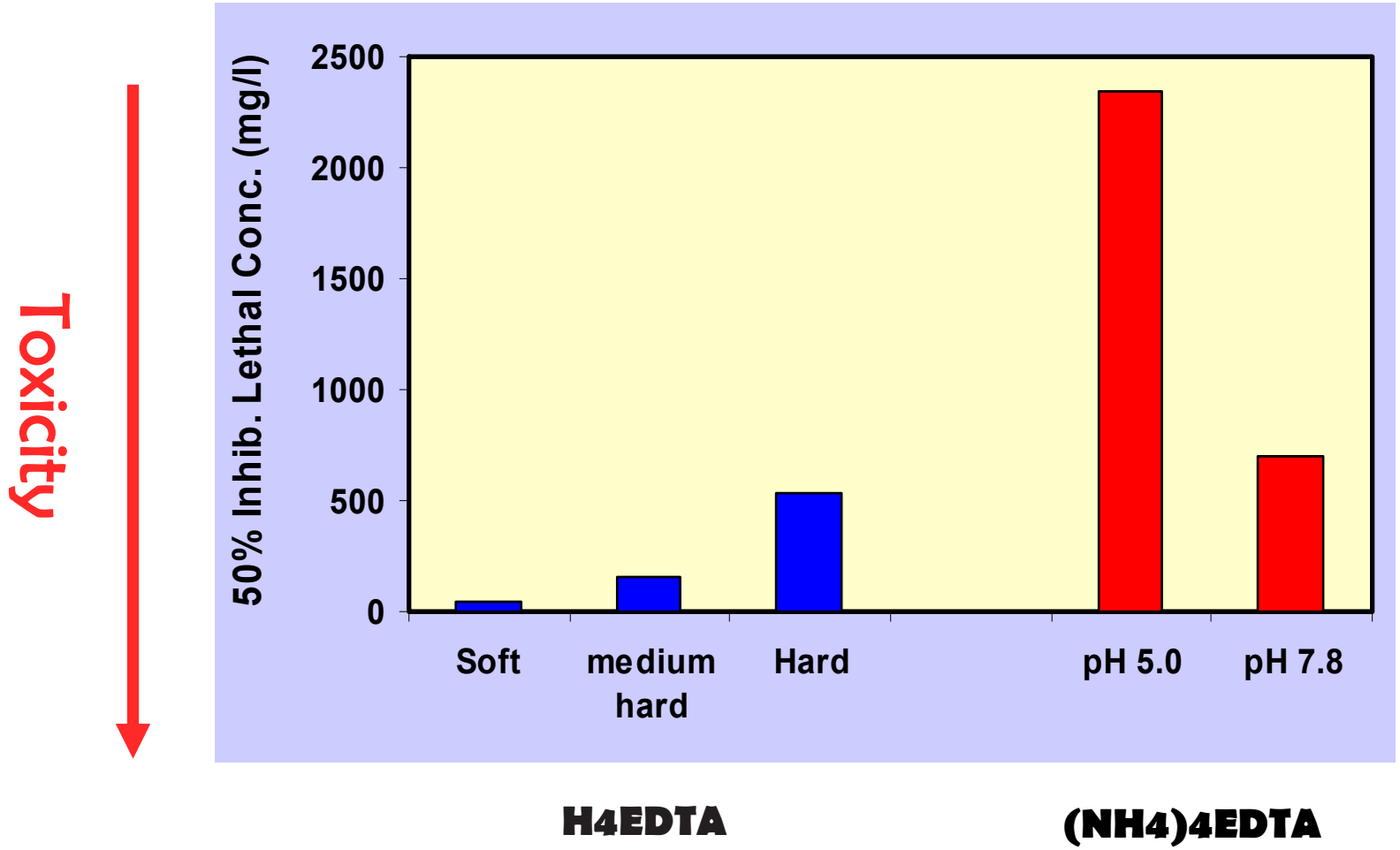


Precipitated metal salt + EDTA → Metal-EDTA (soluble)

$$\text{Metal-EDTA} + Fe^{3+} \rightarrow \text{Fe-EDTA} + \text{Metal}^{+n}$$

(Very stable)
Log K = 10^{25}

Water hardness, pH, Cation conc. Affect Aminopolycarboxylate Toxicity



Acute toxicity (96 h-LC50) of **EDTA** species towards bluegill sunfish (*Lepomis macrochirus*).

Batchelder et al. Bull. Environ. Contam. Toxicol. 1980, 24, 543

Biocides in Semiconductor Manufacturing

CMP

- Prevent growth of bacteria, mold, slime and fungi.

Wet clean processes and plating operations

- Not often used. Extreme pH prevents microbial growth

(Cooling towers and ultra pure water)

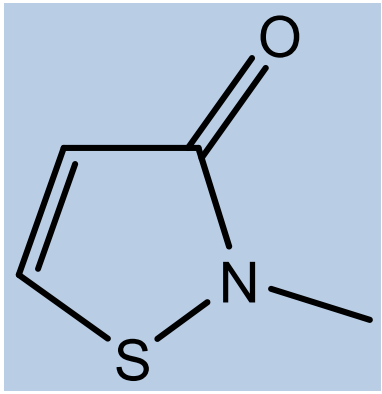
- Used to prevent microbial fouling

Biocides in Semiconductor Manufacturing

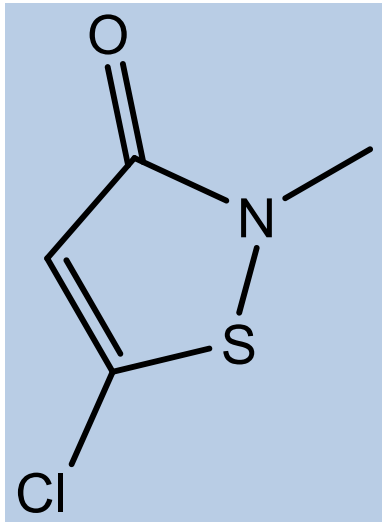
ROHM AND HAAS

- Isothiazolinone derivatives (active ingredients in Kathon®)
- Benzotriazoles (e.g. benzotriazole, tolylbenzotriazole)
- (Quaternary ammonium salts)

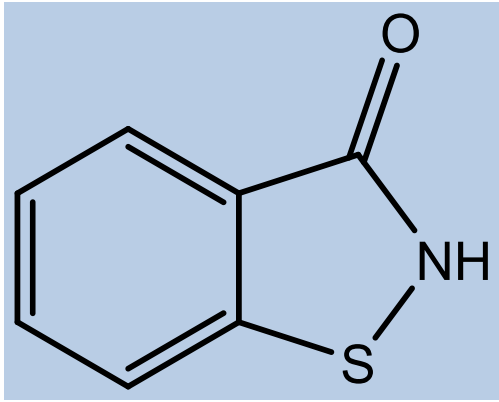
Isothiazolinone biocides



2-Methyl-4-isothiazolin-3-one



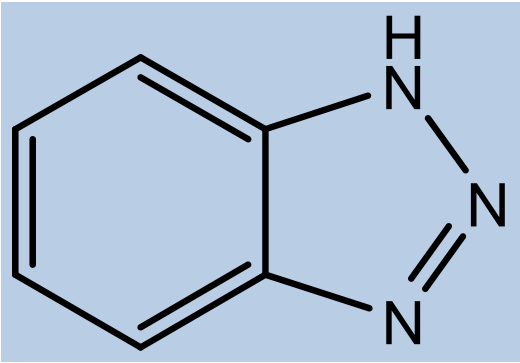
5-Cl-2-methyl-4-isothiazolin-3-one



1,2-Benzisothiazolin-3-one

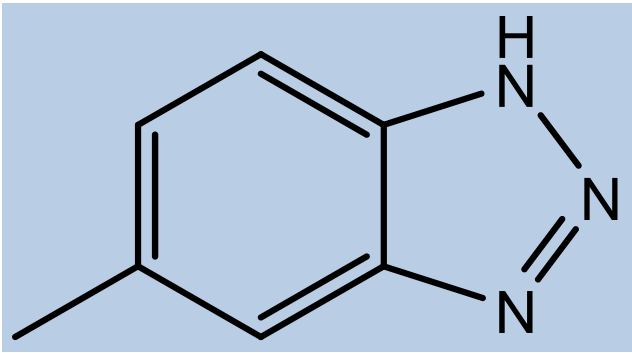
Dichloro-2-n-octyl-4-isothiazolin-3-one

Benzotriazole derivatives



Benzotriazole

(BTA)



Tolyl- benzotriazole

4- or 5-methyl-1H-benzotriazole

Biocides: EHS Characteristics

Compounds are solid at room temperature, low vapor pressure

Exposure: Potential for dermal and inhalation exposure

Hazards

Reactivity:	No
Ignitability:	No
Corrosion:	Yes
Health:	Yes

Health hazard (Acute toxicity)
Isothiazoliones / Benzotriazoles

Biocides: Fate in POWTs

Chelators	Biodegradation	Sorption to sludge	Removal	Microbial toxicity
Isothiazoliones	Yes ?? Benzothiazolones – **No**	Low	No data	**Yes**
Benzotriazoles	**No**	Low	**Low**	No (only at high conc)

Triazoles:
Widespread Environmental Contaminants

Benzotriazole (**BTA**) and **tolylbenzotriazole** (**TT**)
often detected in treated effluents and surface water in USA and Europe

BTA & **TT** detected in effluents of German POWTs
at concs. from below 10 to 100 µg/L (Voutsa et al. 2006).

TT detected in 32% of U.S. streams sampled at conc. > 0.1 µg/L.
Max. and median values were 2.40 and 0.40 µg/L (Kolpin et al. 2002).

Tolyl-benzotriazole in U.S. Surface Waters

(95 organic contaminants monitored in 139 streams across 30 states)

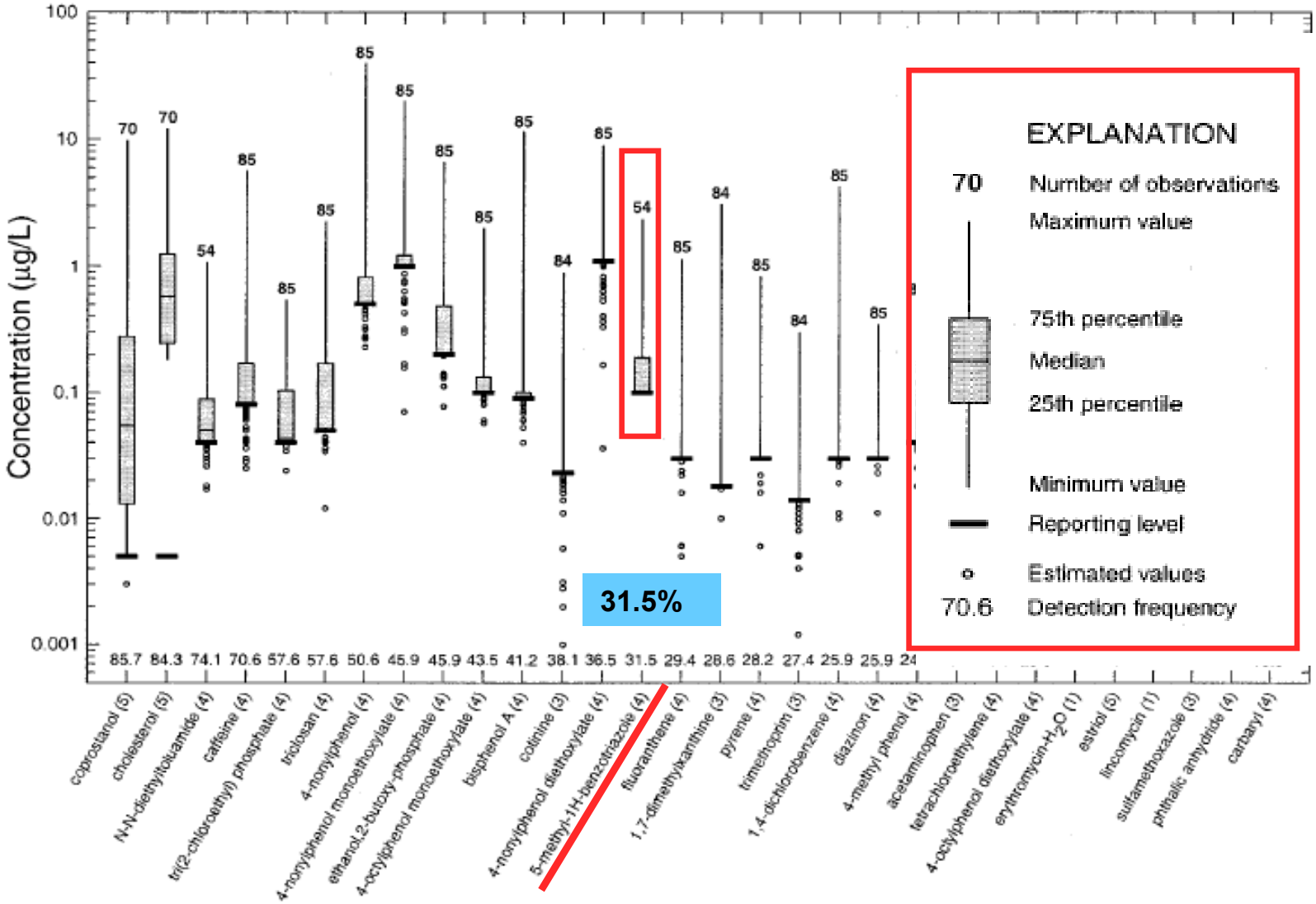
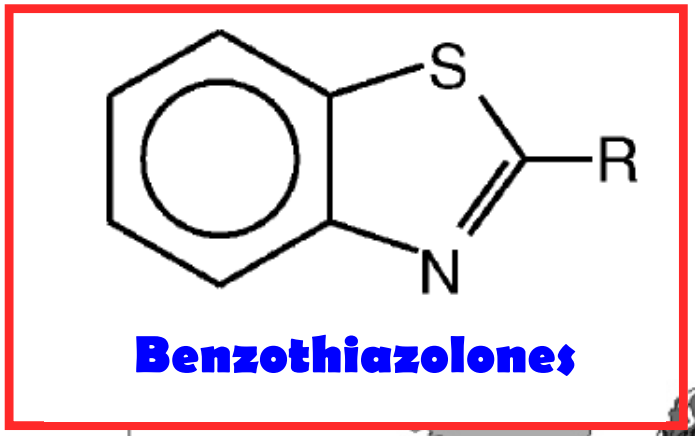
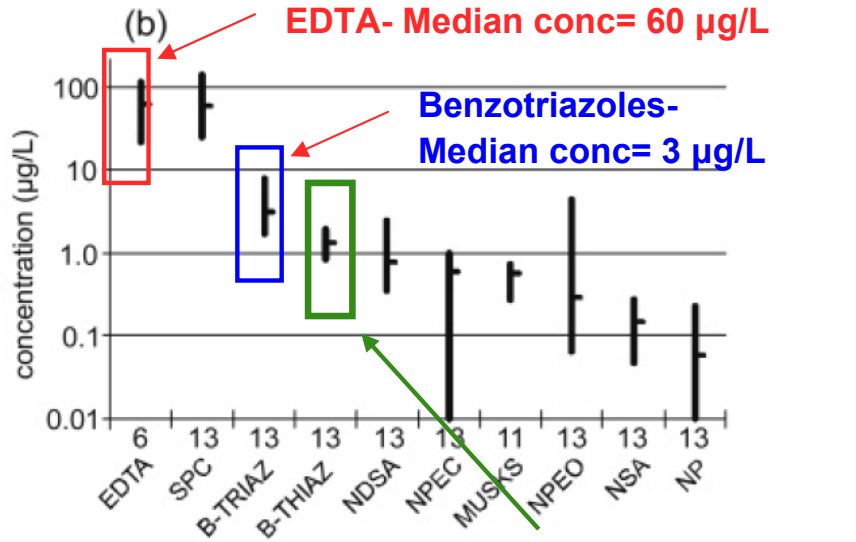


FIGURE 2. Measured concentrations for the 30 most frequently detected organic wastewater contaminants. Boxplots show concentration distribution truncated at the reporting level. Estimated values below the reporting level are shown. Estimated maximum values for coprostanol and cholesterol obtained from Method 5 (Table 1) are not shown. The analytical method number is provided (in parentheses) at the end of each compound name. An explanation of a boxplot is provided in Figure 3.

Kolpin et al.





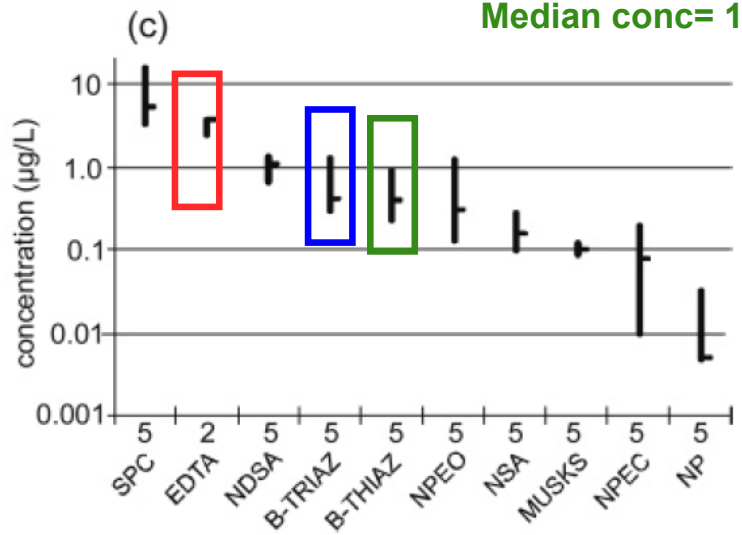
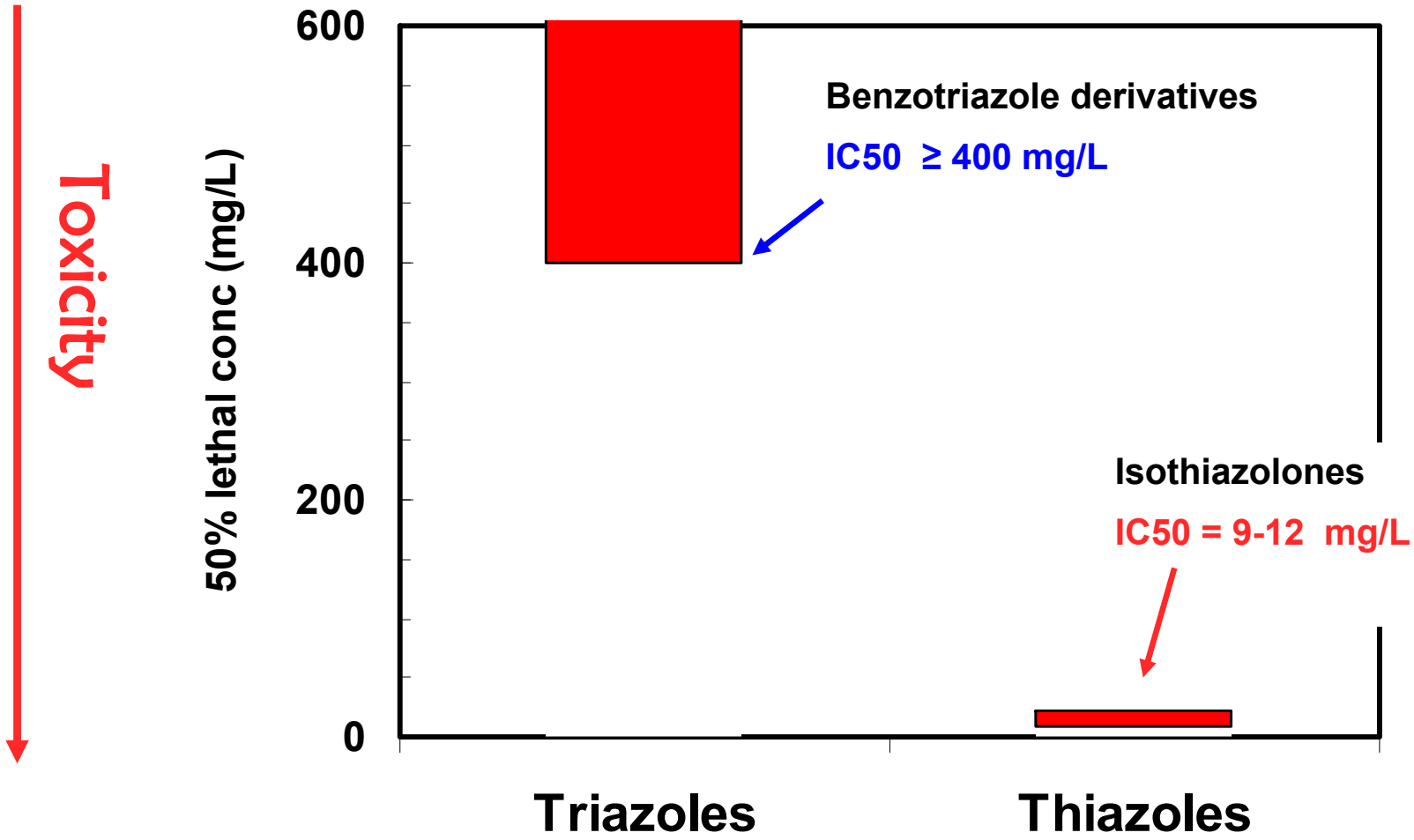


FIGURE 1. (a) Sampling locations for WWTP effluents (black dots) and surface water monitoring (white triangles). Median, 25 and 75 percentile concentrations of polar pollutant classes determined in the monitoring campaign (in μg/L) (b) of 13 effluent samples of eight WWTP in four European countries and (c) in five surface waters of different catchments in Europe. *n* denotes the numbers of samples analyzed.

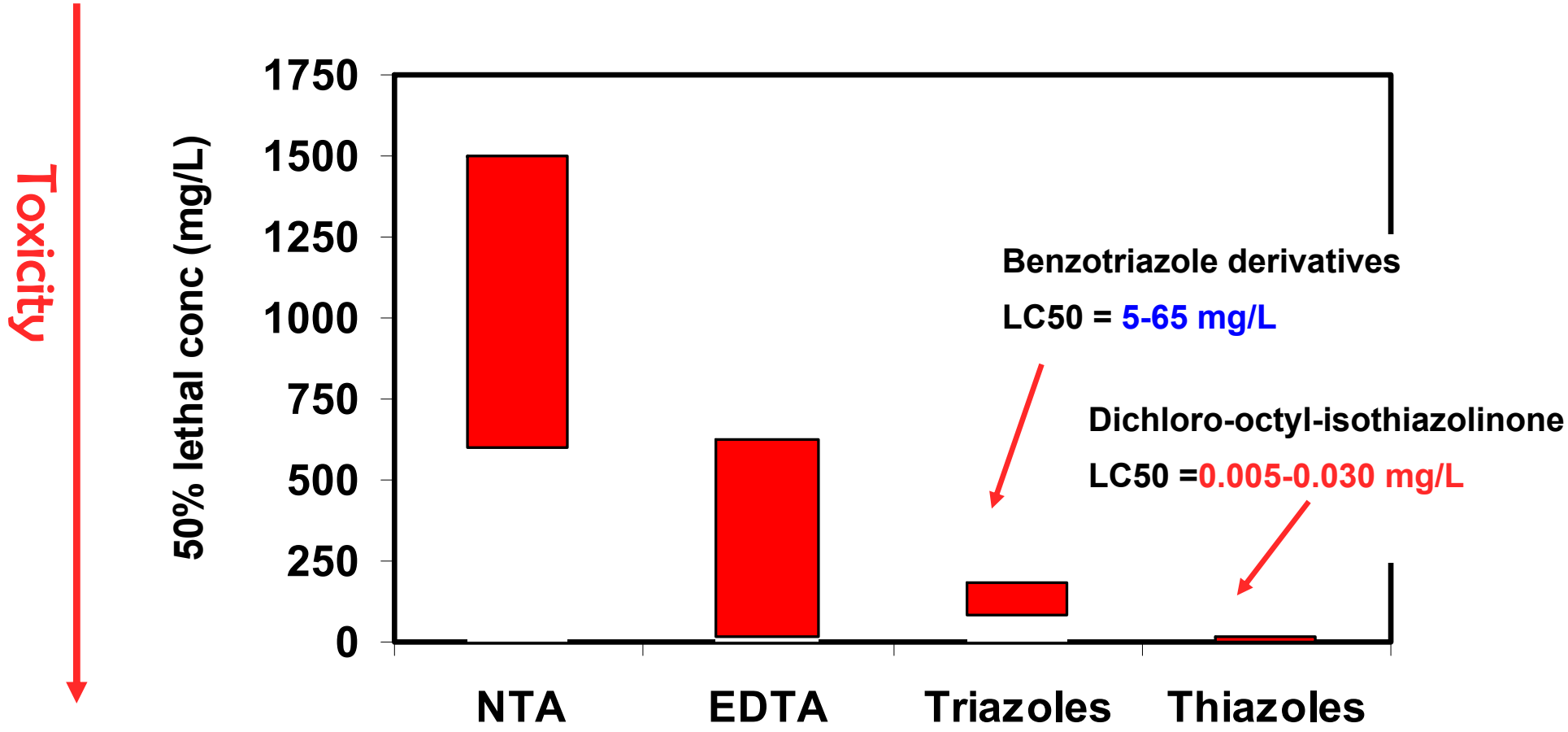
Reemtsma et al. Environ. Sci. Technol. **2006**, 40, 5451-5458

Microbial Toxicity:
Isothiazolones and triazoles



= **BTA is a potent inhibitor of nitrification**

Toxicity of chelators and biocides
to aquatic organisms (water fleas)



Chelators and Biocides of Concern

Compounds	ESH	Aquatic Toxicity	Persistence
Aminopolycarboxylate chelators (EDTA, NTA, etc)	YES*	Moderate/ Low	YES (EDTA)
Benzotriazole derivatives	NO (slight hazard)	LOW	YES
Isothiazoliones	YES	HIGH	YES (Benzothiazoles)

* NTA, DPTA

Acknowledgements

- Steve Trammell and Walter Worth - ISMI/Sematech

- Uyai Umoren – ISMI Intern