

Impact of Fluoride in Wastewater on Publicly- Owned Treatment Works (POTWs)

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Fluoride

- Fluoride is ubiquitous in the environment, it is a component of most types of soils
- Surface water concentrations generally range from 0.01 to 0.3 mg/L
- Fluoride has both beneficial and detrimental effects on human health
 - Eg. protection against dental caries
 - Eg. skeletal and dental fluorosis
- Maximum Contaminant Level (MCL) in Drinking Water: **4 mg F⁻/L**

Secondary Drinking Water Standard
(recommended, not enforceable level): **2 mg F⁻/L**

Sources of Fluoride in the Aquatic Environment

- Fluoride is often present in semiconductor manufacturing effluents at relatively high levels

Max. conc. (mg F⁻/L): 4.7 - 72.0 mg/L; Avg Conc. (mg/L): 4.3 - 26.8 mg/L

(Data from 9 Manufacturing Sites, Sematech)

- Fluoride is also found in other industrial effluents, e.g.:

Aluminum smelter effluents
Phosphate fertilizer plants
Plants producing fluoride chemicals

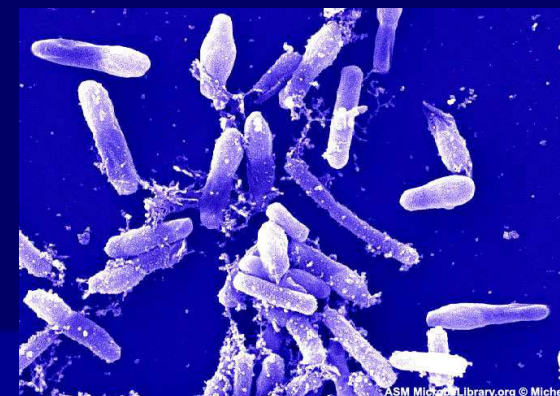
- Other sources of fluoride into the aquatic environment include:

Weathering and dissolution of minerals
Fluoridation of drinking water (0.7-1.2 mg F⁻/L)



Literature review

Key findings for FLUORIDE:

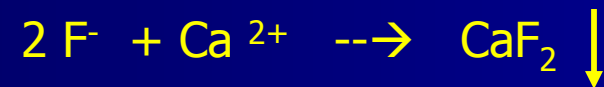
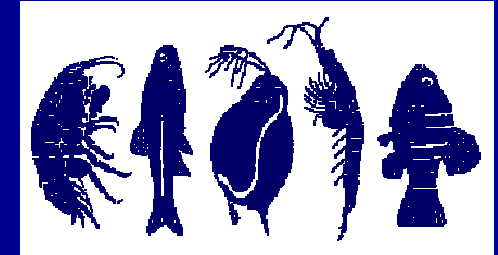


- Fluoride can inhibit the activity of various enzymes (eg. phosphatases, enolases, hexokinase) and interfere with metabolic processes such as glycolysis and protein synthesis.
- Information is lacking on the toxic effects of fluoride to microorganisms in wastewater treatment systems. To date, studies have only evaluated nitrification processes in detail. Fluoride is only inhibitory to nitrification at very high concentrations.
(50% inhibition at 630 to 2000 mg/l or higher).
- Numerous studies concerned with the toxicity of fluoride to oral bacteria due to the interest in fluoride by dentistry. Fluoride inhibits cell growth and fermentation in a variety of oral bacteria at moderate to high concentrations.
(50% inhibition at 5 to 1600 mg/l).

Literature review

Key findings for FLUORIDE

- Fluoride is only lethal to most aquatic organisms at relatively high concentrations (50% inhibition at 100-800 mg F-/L)
- Exposure to low F levels (0.5-1.5 mg/L) can cause adverse effects, affecting reproduction, behavior, etc.
- Precipitation and complexation reactions can lead to considerable removal of soluble fluoride in wastewater treatment systems and natural aquatic environments, resulting in decreased toxicity . E.g.

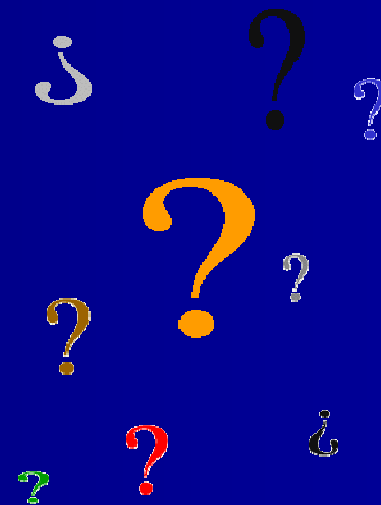


Toxic Impact of Fluoride on Biological Wastewater Treatment

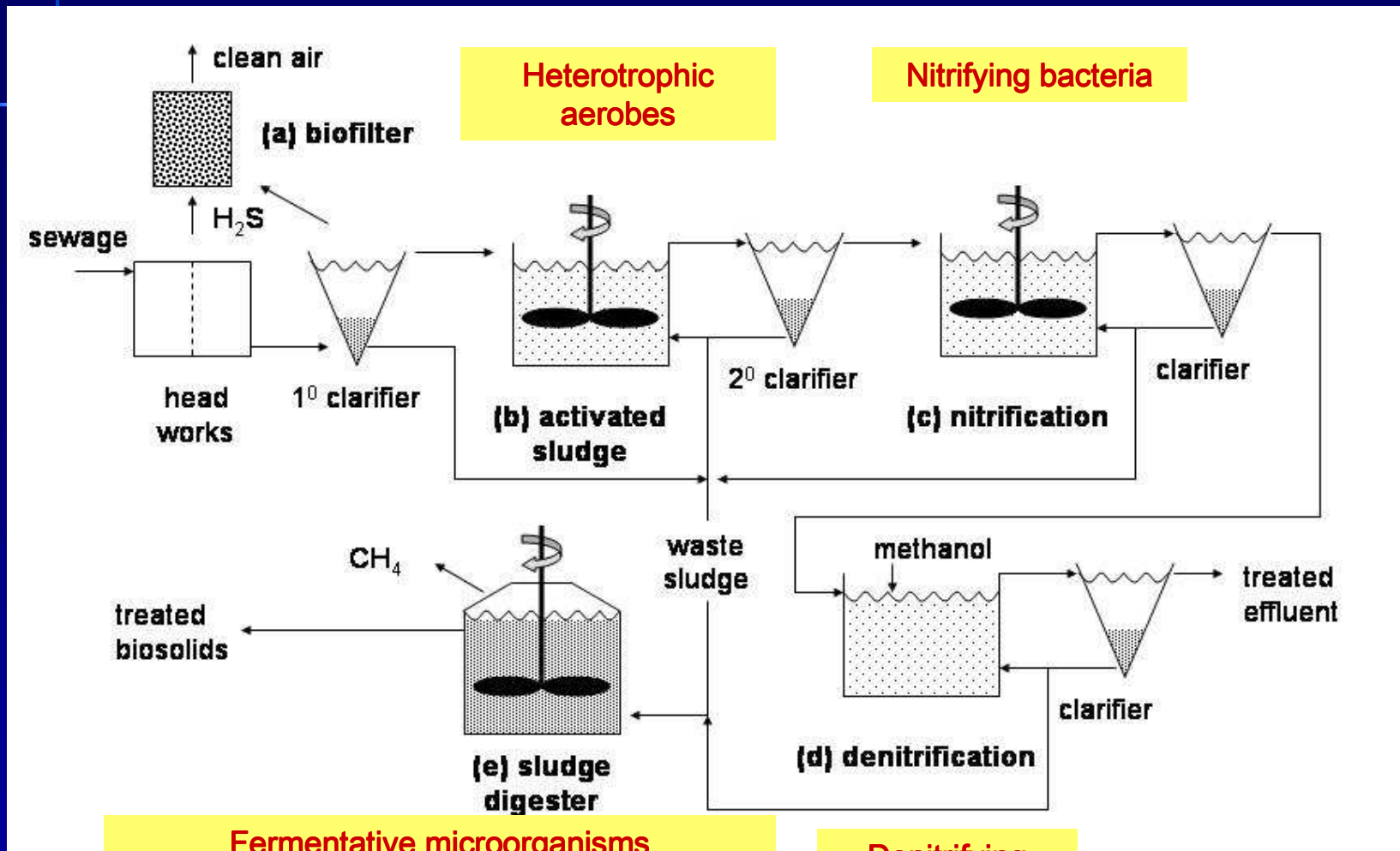
- Growing concern about potential toxic effects of fluoride towards microorganisms in wastewater treatment plants (WWTP) and higher aquatic organisms.



- Virtually no one has studied the toxicity of fluoride to WWTP bioprocesses before, only nitrification was looked at previously



Unit processes and key microbial populations in a typical municipal wastewater treatment plant



Heterotrophic aerobes

Nitrifying bacteria

Fermentative microorganisms

Denitrifying bacteria

Methanogens –
Mesophilic (30-35°C) & Thermophilic (55-60°C)

Anaerobic Treatment Processes



Sludge Digesters

Mesophilic (30-35°C) and Thermophilic (55-60°C)



Wastewater Treatment Bioreactors

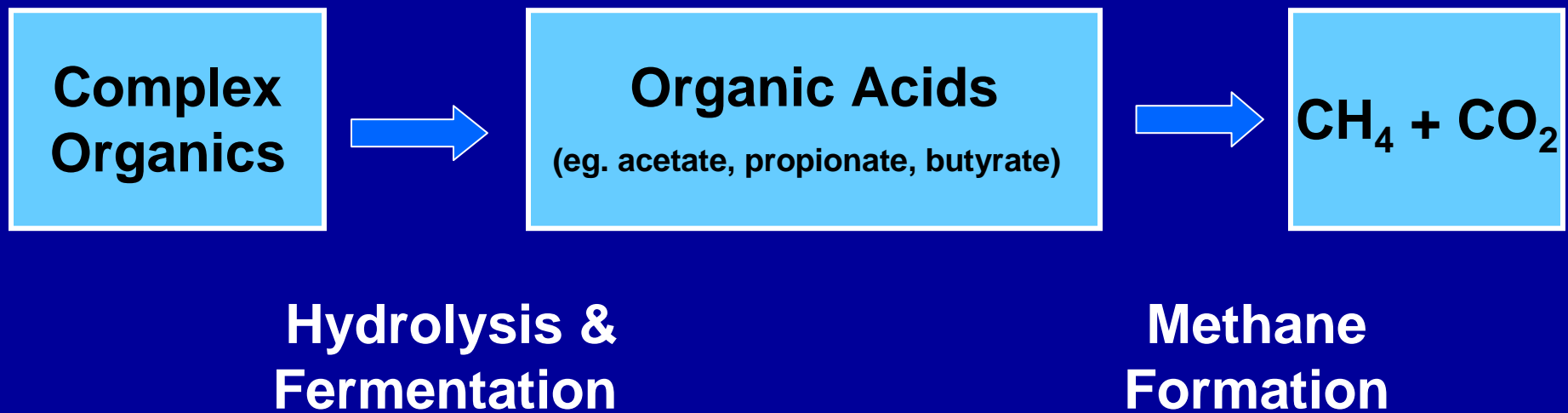
Gist Brocades (yeast, pharmaceuticals), The Netherlands

Objectives Anaerobic Digestion Biosolids

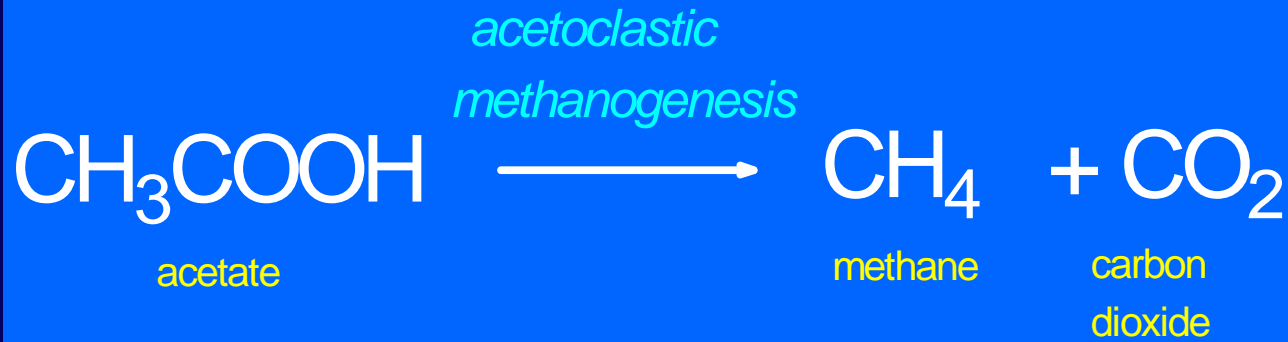
- Stabilize excess sewage sludge
- Methane production (useful energy)
- Improve Sludge Dewatering
- Reduce pathogens



Anaerobic Pathways - Two Stage Concept



Methanogenic Reactions

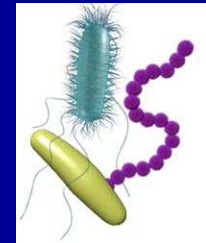


Methane flare at a WWTP

Objectives

Determine the inhibitory effect of fluoride towards:

- Main microbial populations in wastewater treatment systems.
- Common effluent monitoring species
(water fleas and fathead minnows)



Daphnia spp



Fathead minnow

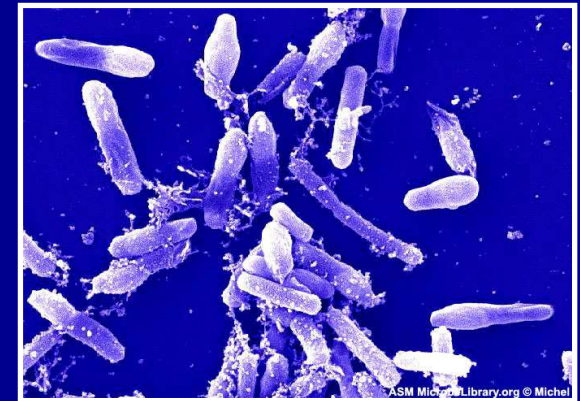
Assessment of Fluoride Inhibition

Methodology:

- Microbial toxicity (UofA)

- a) Standardized batch bioassays

- b) Short-term continuous bioreactor studies
(*most sensitive microbial population*)



- Acute toxicity to fathead minnows & daphnids (ecotoxicology lab)

EPA standard methods #2002.0 and #2000.0

Microbial Inhibition Assays

Set Up

- Medium with nutrients/minerals and substrate
- Inoculum
- Headspace N₂/CO₂ (80/20) or Air
- 30°C and 55°C

Controls

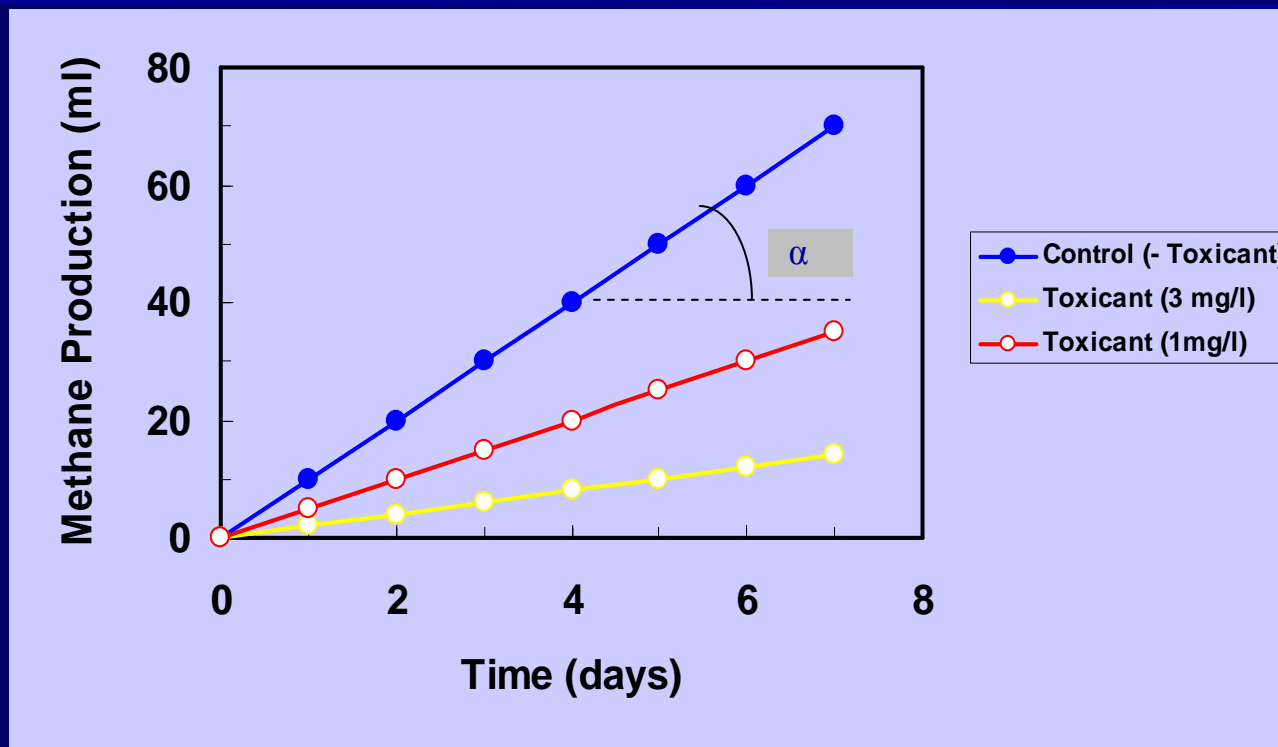
Inoculum - medium lacking fluoride

Treatments

Inoculum - medium with increasing concentrations of fluoride

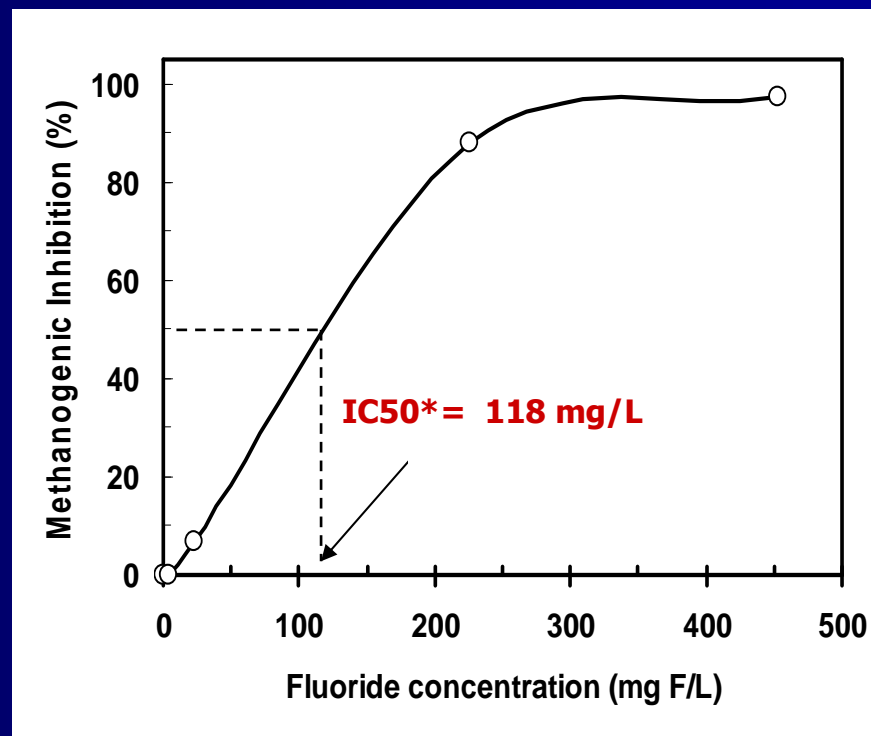


Time Course of Methane Production in the Presence and Absence of a Toxicant



$$\text{Activity (\% of Control)} = 100 * \text{Activity}_{\text{treatment}} / \text{Activity}_{\text{control}}$$
$$\% \text{ Inhibition} = 100 - \% \text{ Activity}$$

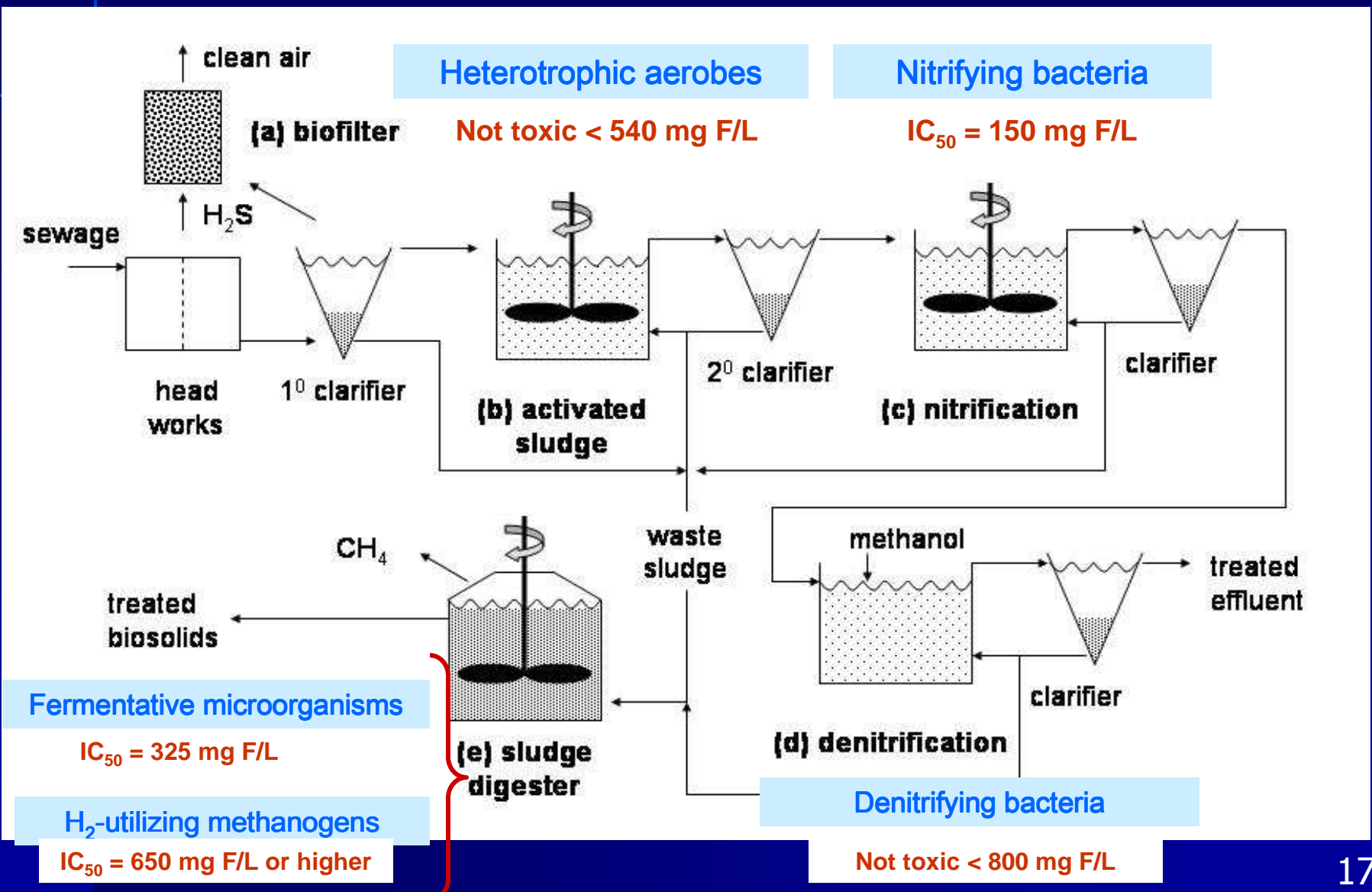
Calculation of the Inhibitory Concentrations (eg. IC_{50})

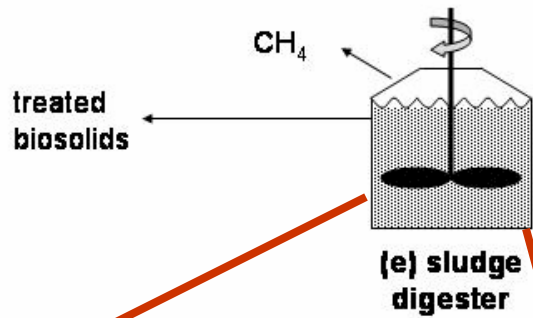


* IC_{50} = Concentration causing 50% microbial inhibition

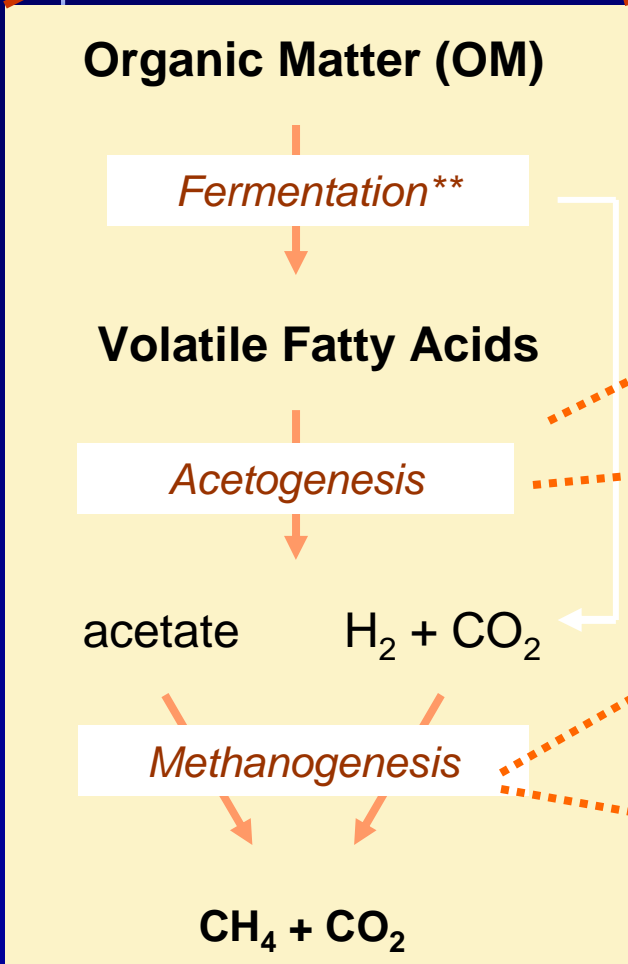
Microbial Populations in Municipal Wastewater Treatment Plants

Showing HIGH TOLERANCE to FLUORIDE





Microbial Populations in Anaerobic Processes showing LOW TOLERANCE to FLUORIDE



Butyrate-utilizing microorganisms

$\text{IC}_{50} = 29 \text{ mg F/L}$

Propionate-utilizing microorganisms

$\text{IC}_{50} = 35 \text{ mg F/L}$

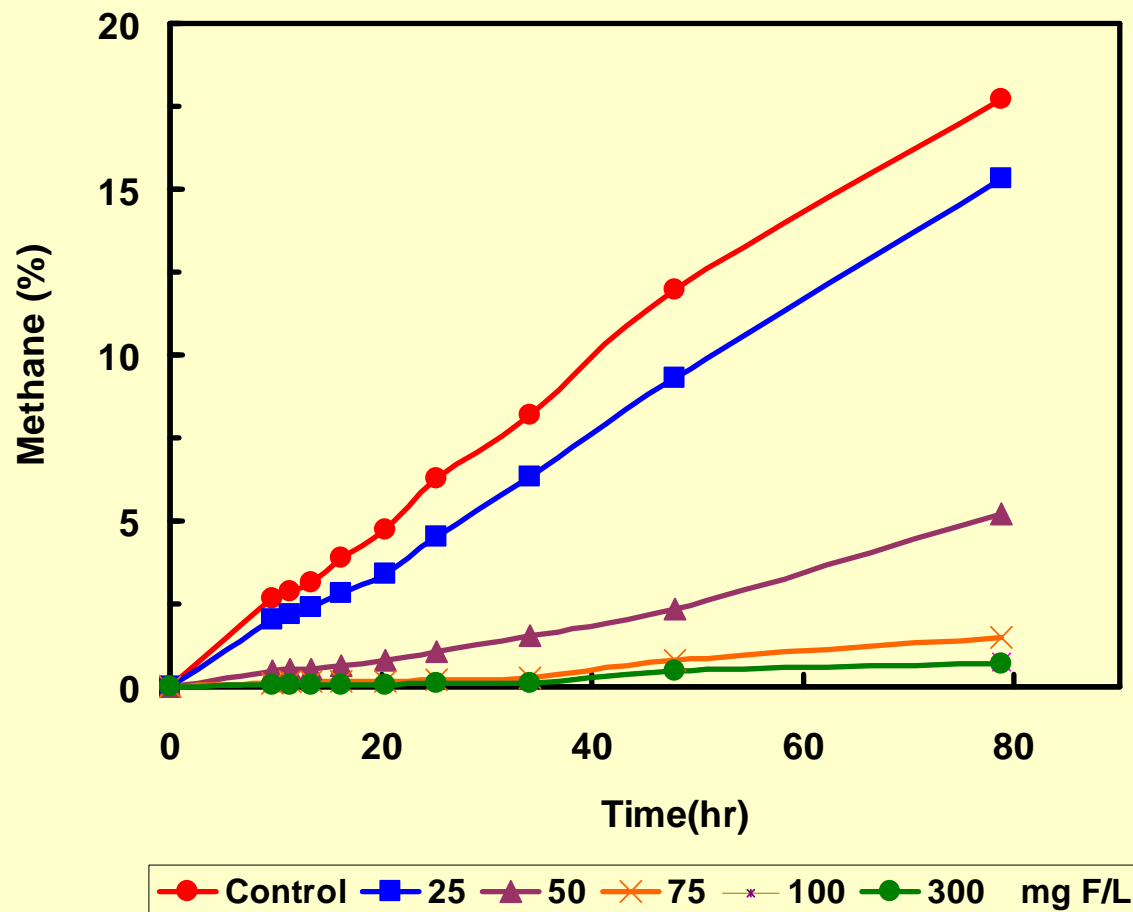
Acetate-utilizing methanogens - mesophilic

$\text{IC}_{50} = 26-54 \text{ mg F/L}$

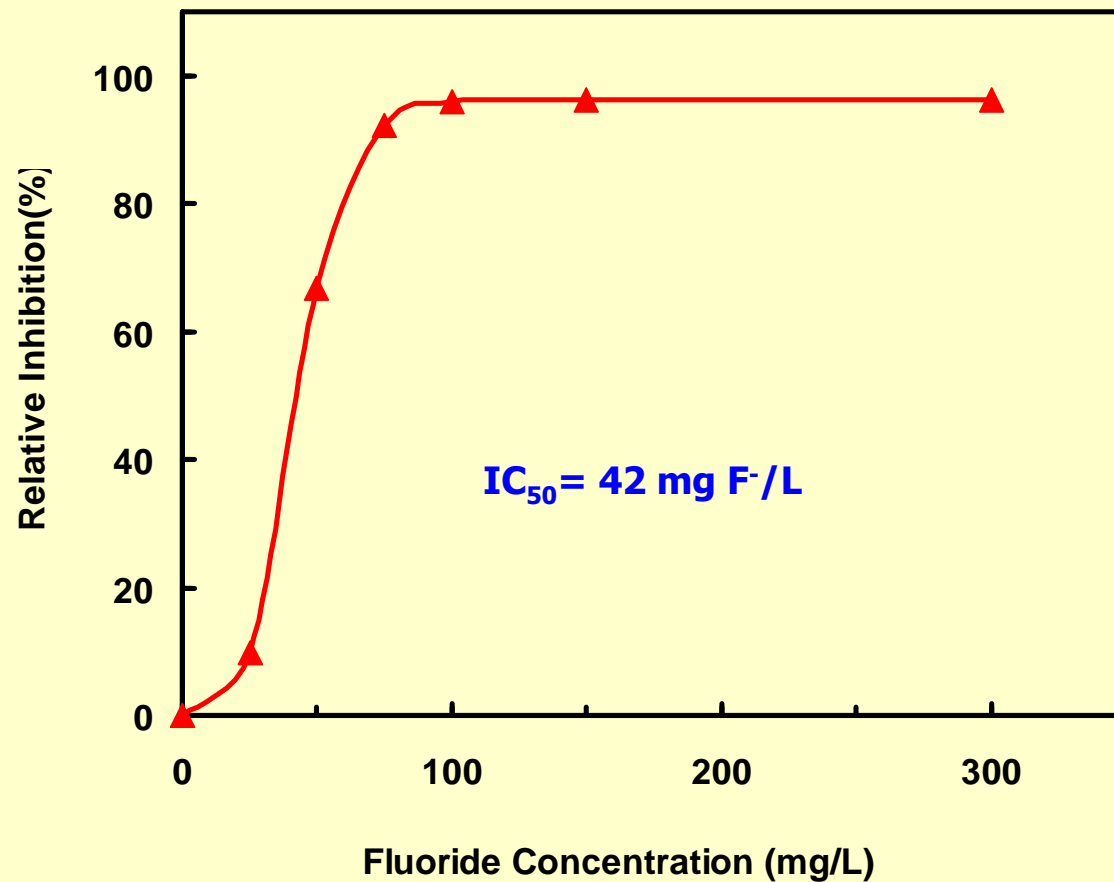
Acetate-utilizing methanogens - thermophilic

$\text{IC}_{50} = 42 \text{ mg F/L}$

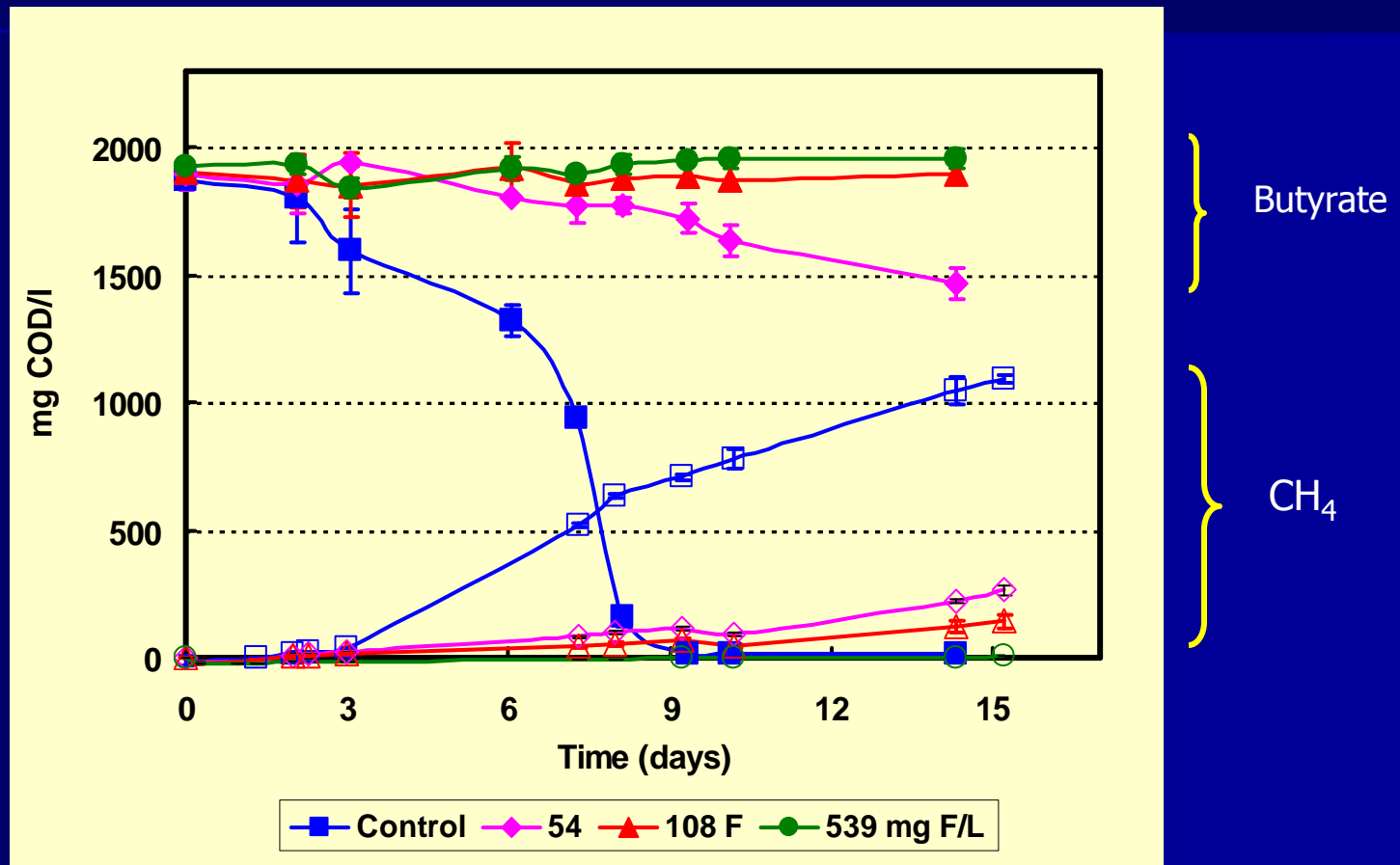
Inhibition of Thermophilic Acetate-Utilizing Methanogens by Fluoride



Inhibition of Thermophilic Acetate-Utilizing Methanogens by Fluoride



Inhibition of Butyrate-Utilizing Microorganisms by Fluoride

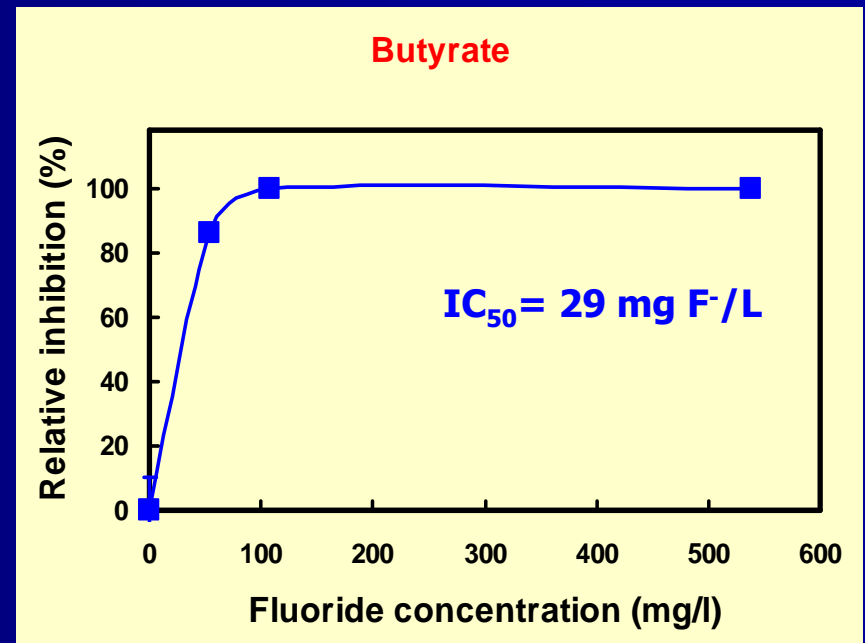
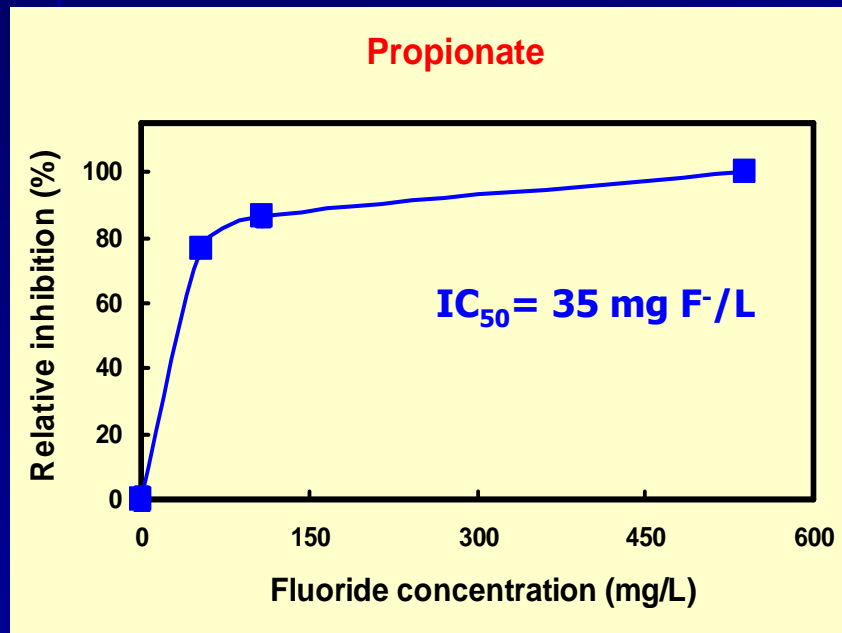


Butyrate

Acetate

Methane

Inhibition of Propionate and Butyrate-Utilizing Microorganisms by Fluoride



Toxicity of Fluoride to Methanogens: Significance



Anaerobic sludge digesters

- Acetate (C2), propionate (C3) and butyrate (C4)-utilizing microorganisms appear to be inhibited at concentrations close to those in semiconductor effluents
- These microorganisms are important in anaerobic sludge digesters.

Fluoride: Acute Effects on Biomonitoring Species

96-hours LC₅₀

FLUORIDE

Fathead minnows
(*Pimephales promelas*)

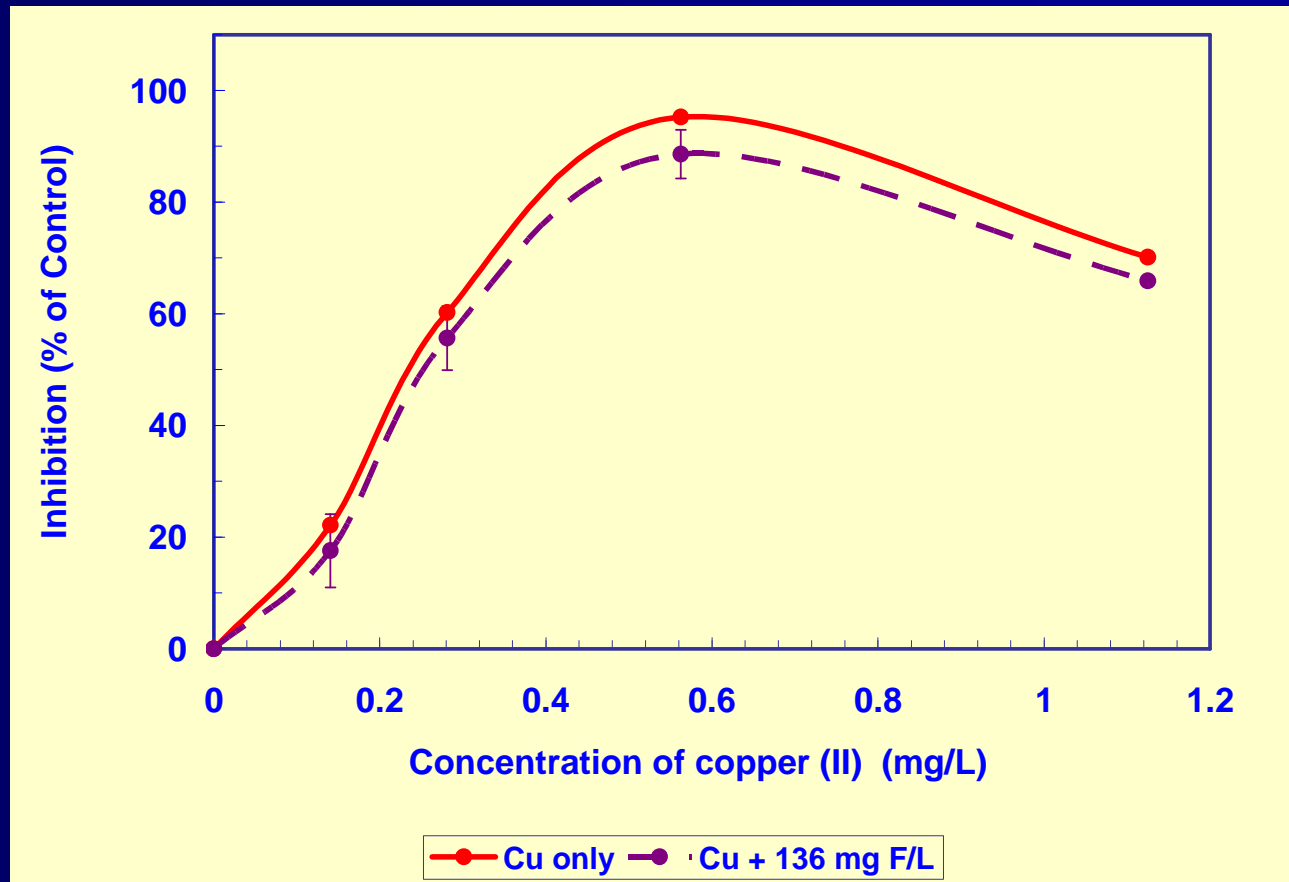
442 mg/L F⁻

Water fleas
(*Ceriodaphnia dubia*)

188 mg/L F⁻

Potential Synergistic/Antagonistic Interactions between F⁻ and Cu(II):

Microtox results



Conclusions

- Inhibitory effect of fluoride varies considerably depending on the microbial population.
- Only acetate, propionate and butyrate-utilizing microorganisms appear to be inhibited at concentrations in the range of those found in semiconductor effluents. Anaerobic sludge digestion, only process which may be impacted, needs to be studied in more detail.

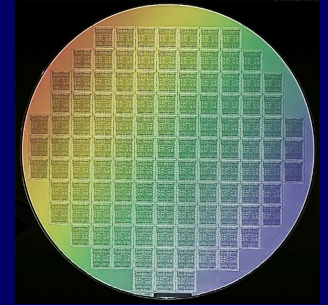
= IC50: 26 - 54 mg/l

= Fluoride in semiconductor effluents* (Data from 9 Manufacturing Sites, Sematech)

Max. Conc: 4.7 - 72.0 mg/L / Avg. Conc: 4.3 - 26.8 mg/L

- Fluoride did not have synergistic/antagonistic effects on copper toxicity (Microtox bioassay)
- The composition of municipal wastewater can affect the inhibitory effect of fluoride (Concn of toxic species (soluble form) can decrease by precipitation /complexation).

Future Activities



- Detailed investigation of the inhibitory effect of fluoride on acetate-, propionate- and butyrate-utilizing anaerobic microorganisms, including continuous bioreactor studies.

Acknowledgments

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