Perchlorate Degradation in Bench- and Pilot-Scale Ex-situ Reactors

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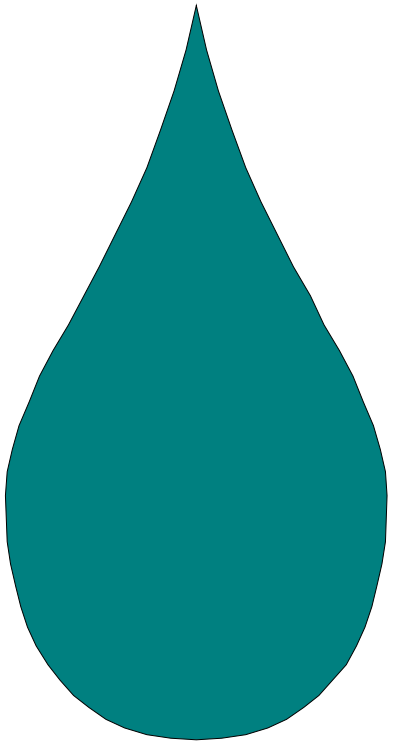
Perchlorate Degradation: Topics

- **Abundance of perchlorate degrading bacteria.**
- Bacterial isolate used in tests: KJ
- Bench-scale reactors: Acetate

  H_2
- Comparison of rates in bioreactors
- Pilot-scale reactor test

Are perchlorate-respiring bacteria abundant in nature?

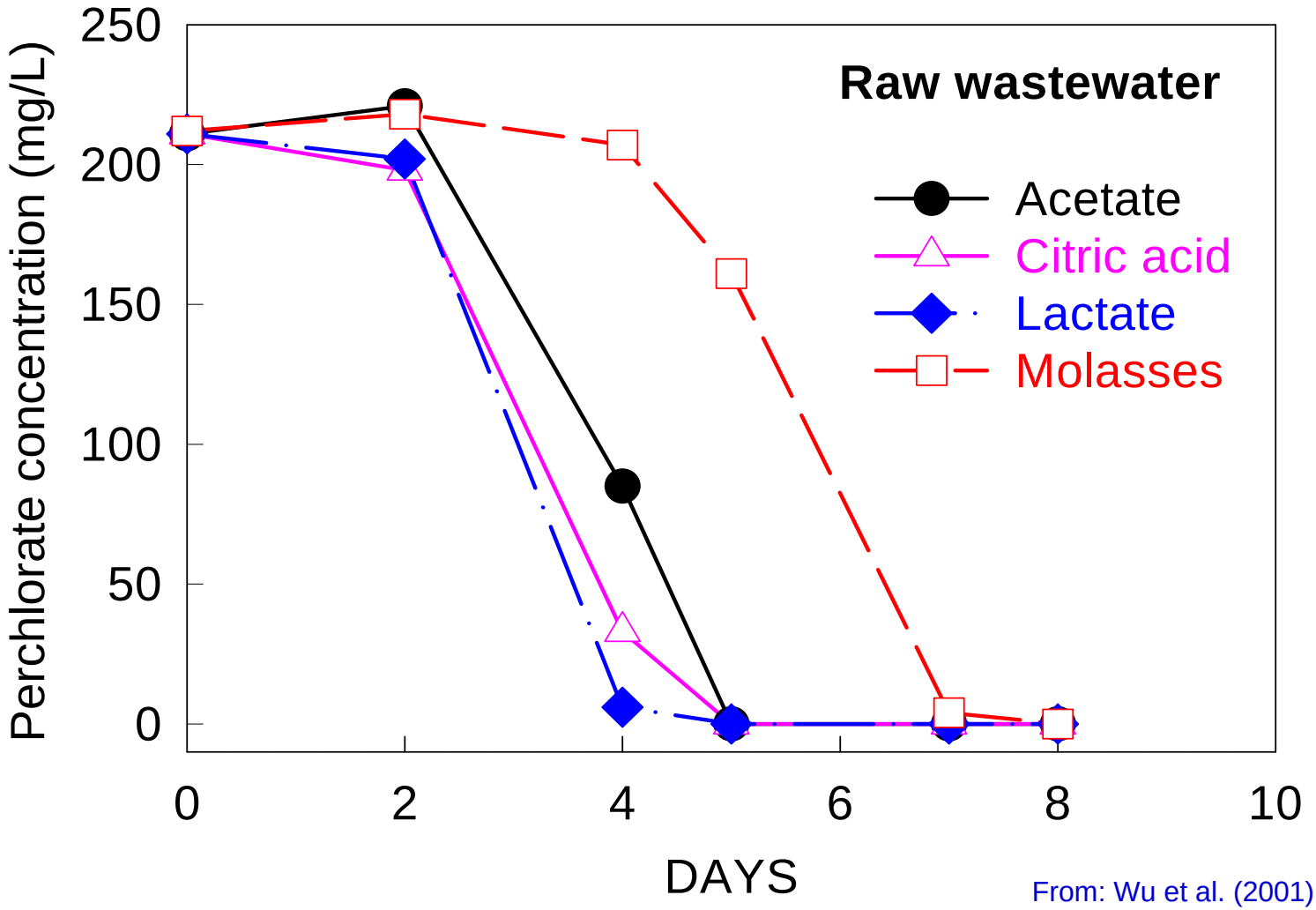


One milliliter (1 mL) of water (about one teaspoon) contains:

- >10^6 bacteria
- < 1 perchlorate-reducing microbe (PRM)

Wastewater

Total cells = 8.9×10^7 per ml



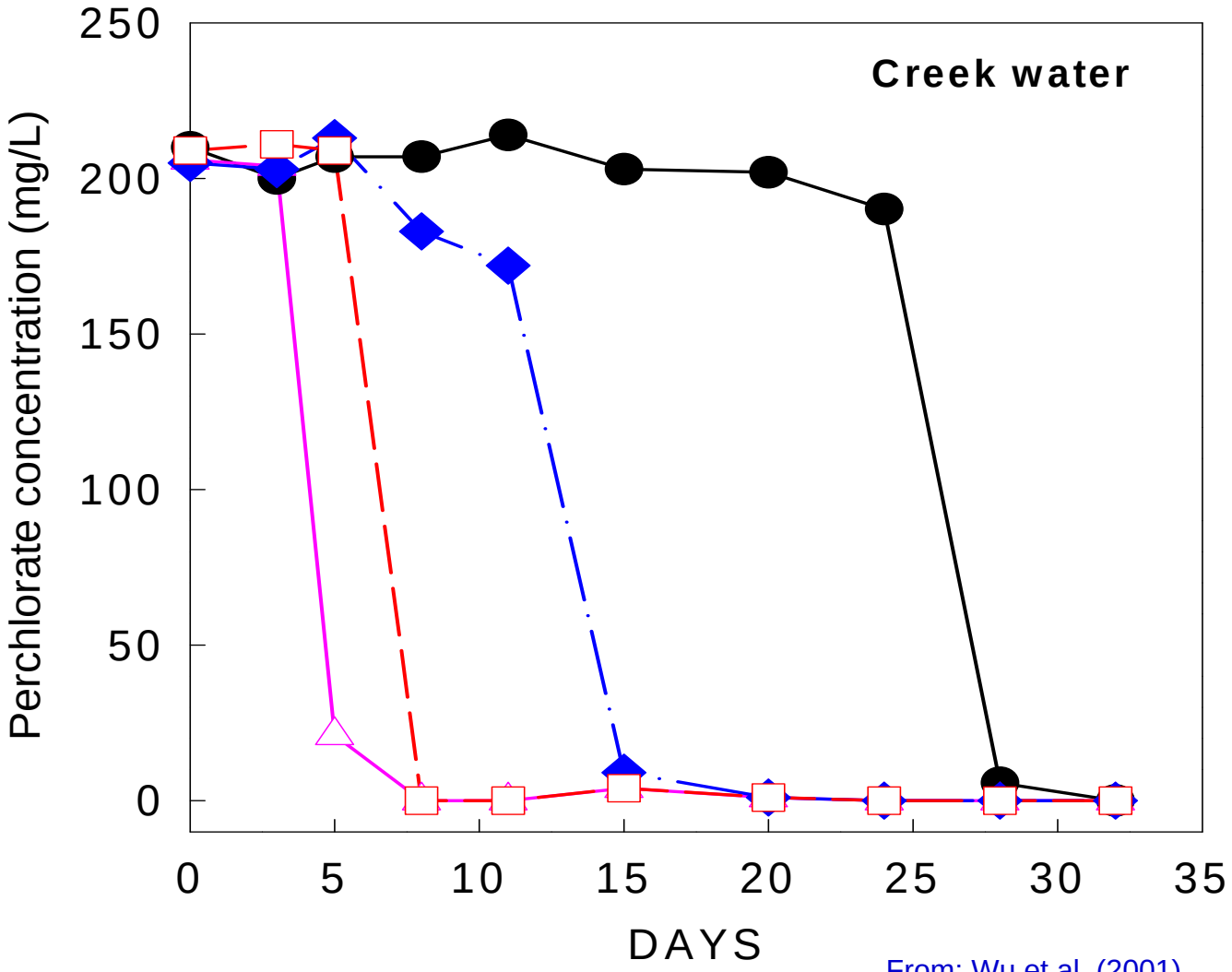
From: Wu et al. (2001)

B. Logan

Creek water

Total cells: 4.9×10^5 per ml

Citric acid
Molasses
Lactate
Acetate

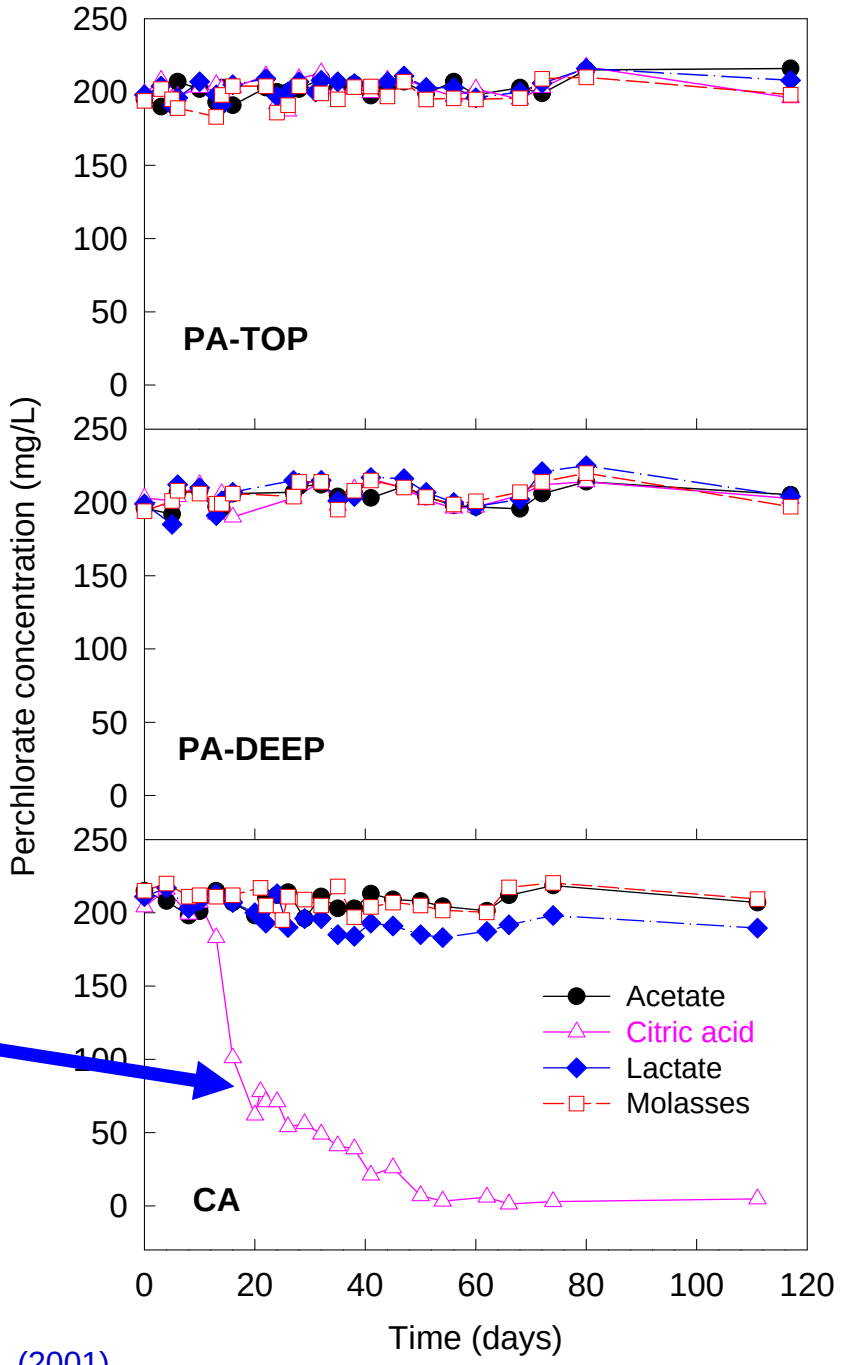


From: Wu et al. (2001)

Unexposed Soils

2 gram samples

The citrate sample was positive on the 3 other substrates as well

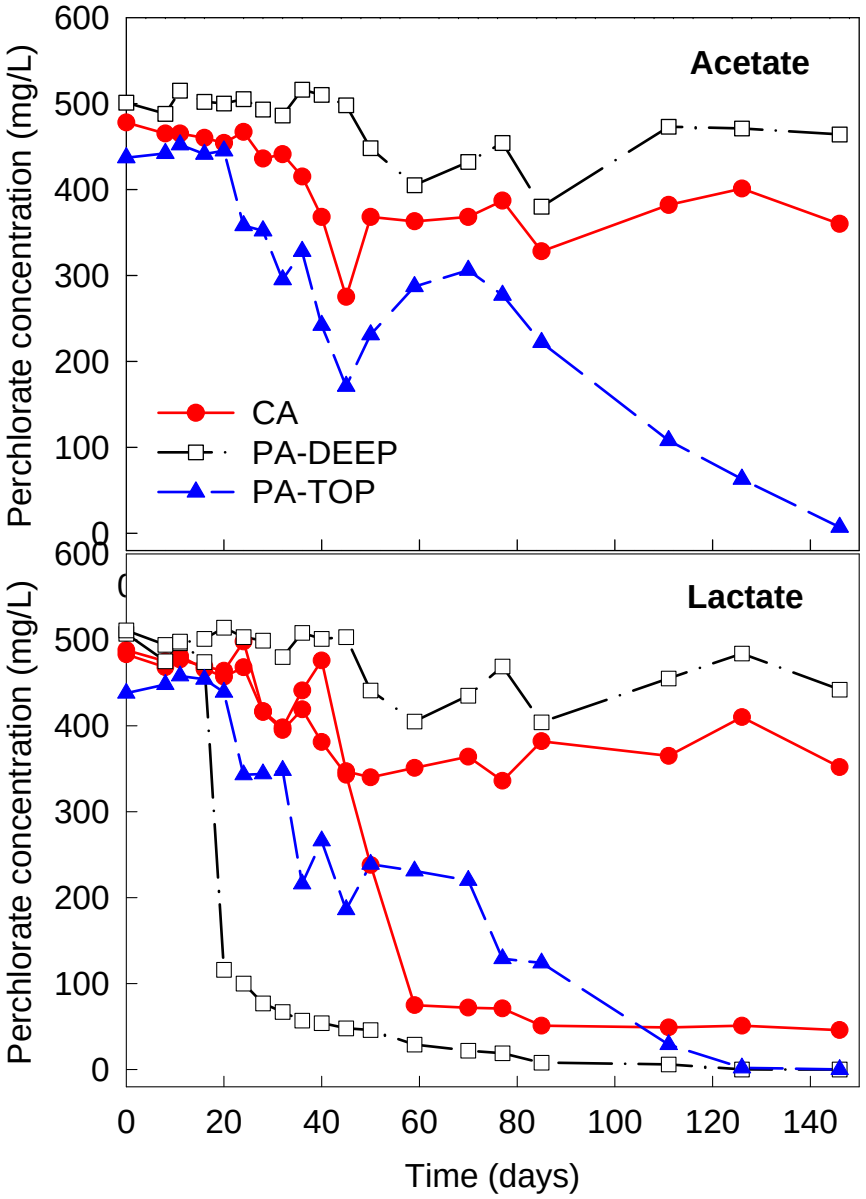


From: Wu et al. (2001)

Unexposed Soils

100 gram samples

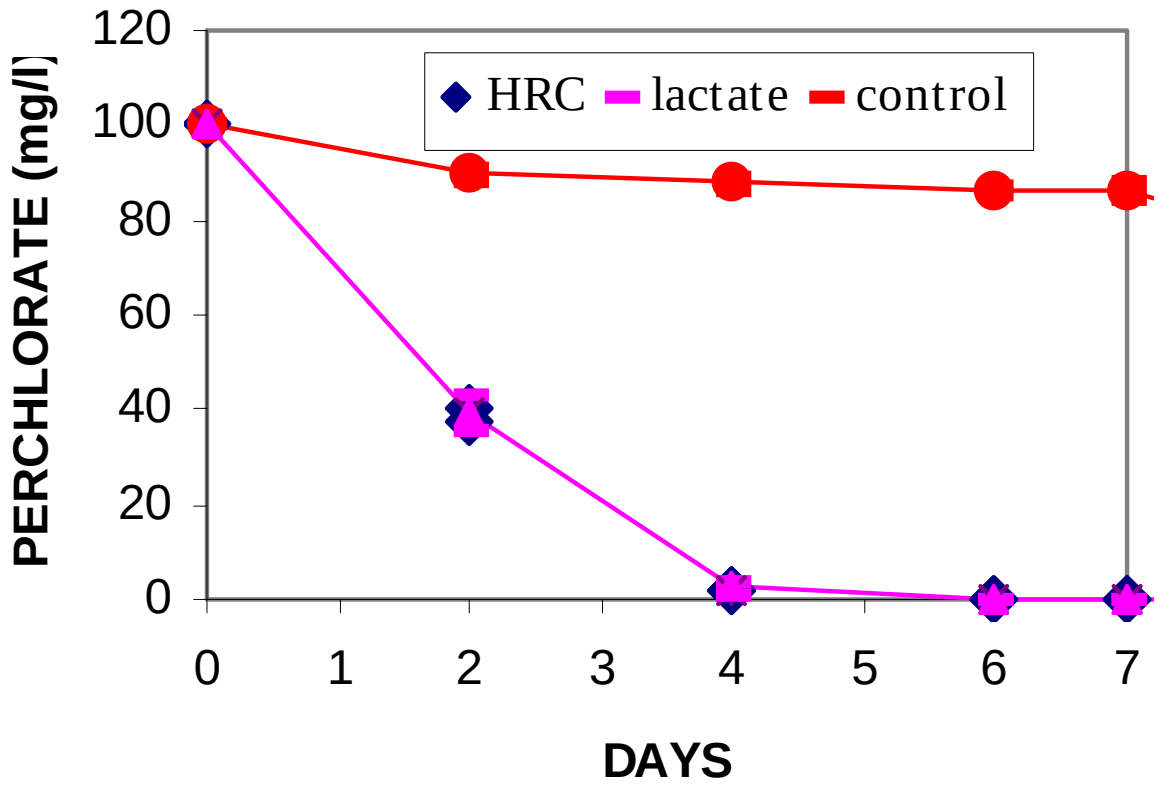
Many soils showed perchlorate degradation when a larger sample mass was used



From: Wu et al. (20

Perchlorate-contaminated soil

Previous exposure of a soil to perchlorate results in rapid Perchlorate degradation



From: Wu et al. (2001)

PRM Abundance: observations

- PRMs present in natural waters at ~1000/10^9
- PRMs in "pristine" soils, that have no evidence of perchlorate contamination: ~1/10^9
- At sites where perchlorate is present, have an abundant perchlorate reducing population, ~100/10^9

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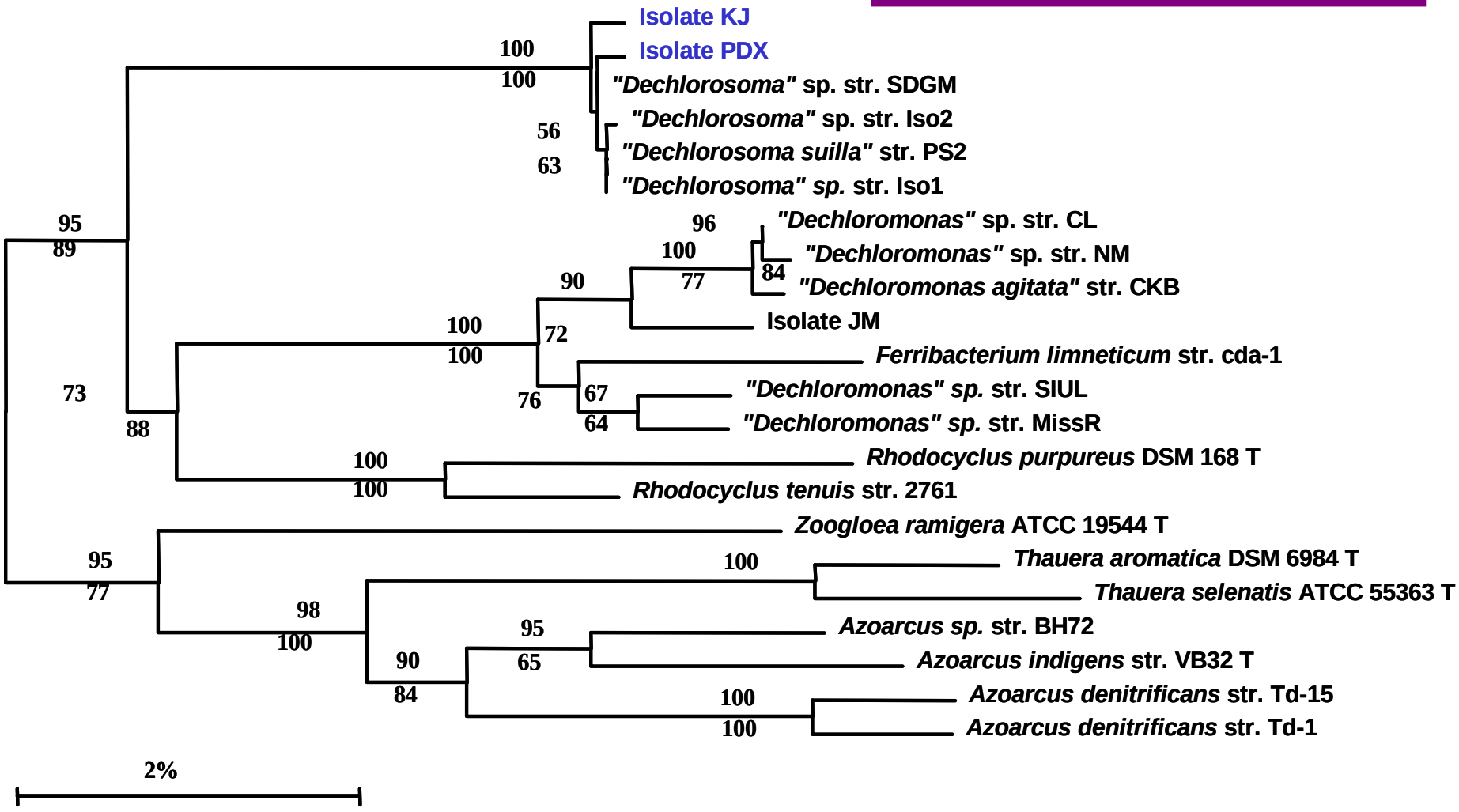
Phylogentic analysis of KJ

(courtesy of Dr. Ian Head, Univ. of New Castle)

Classification:

Dechlorosoma sp. KJ



From: Logan et al. (2001)

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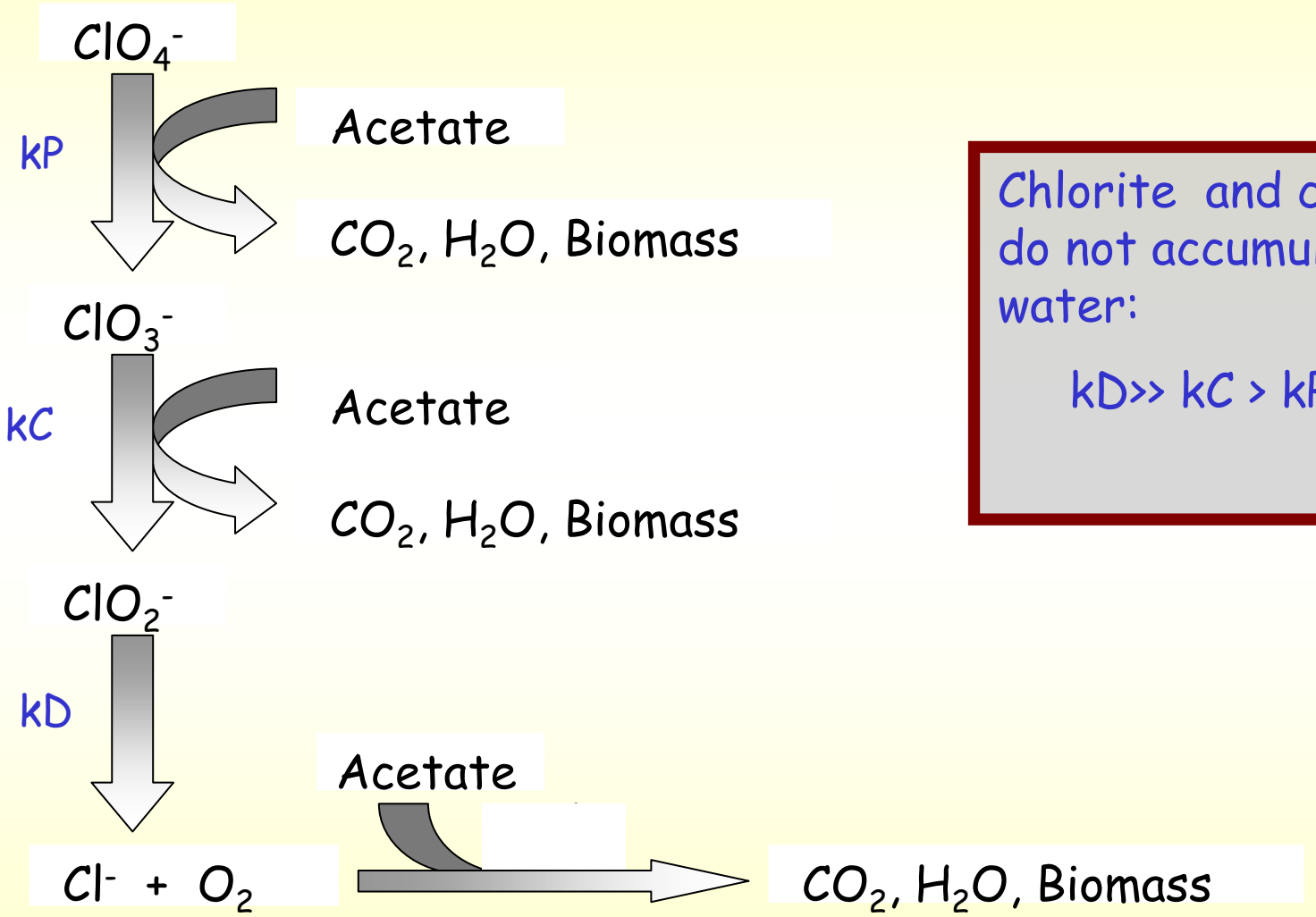
Perchlorate Reducing Pathway

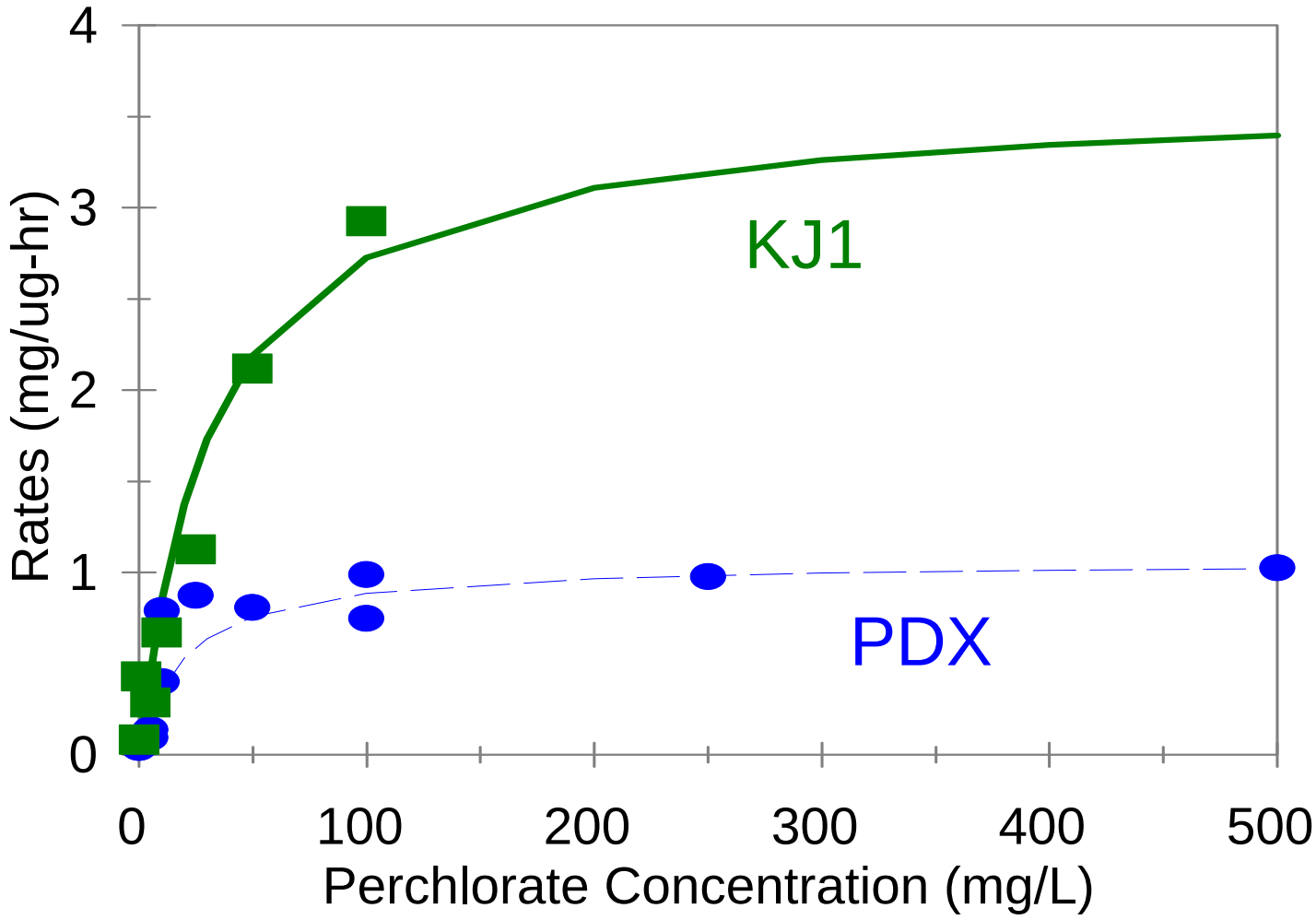


Chlorite and chlorate do not accumulate in water:

kD>> kC > kP

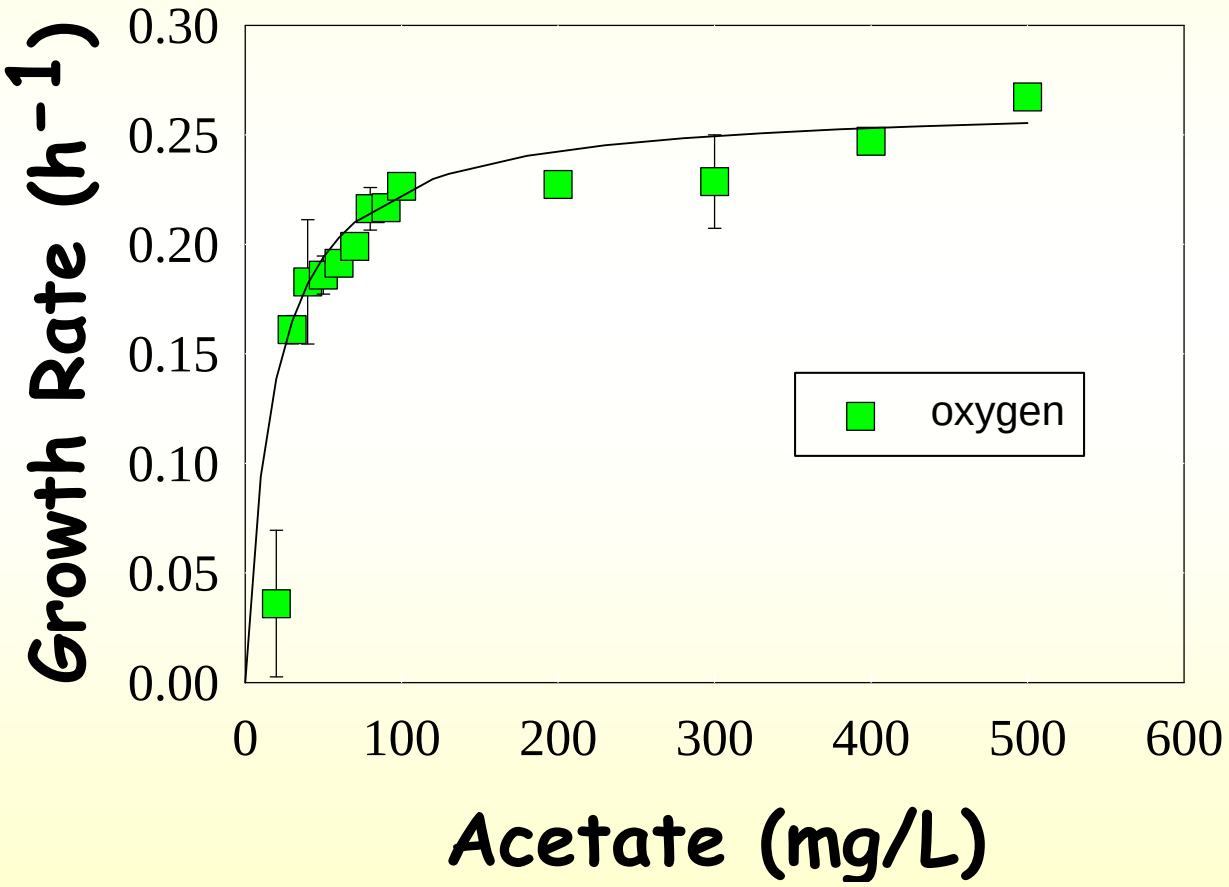
KJ Perchlorate kinetics: K_s=33 mg/L

(lactate grown cell suspensions)



From: Logan et al. (2001)

Substrate kinetics: acetate



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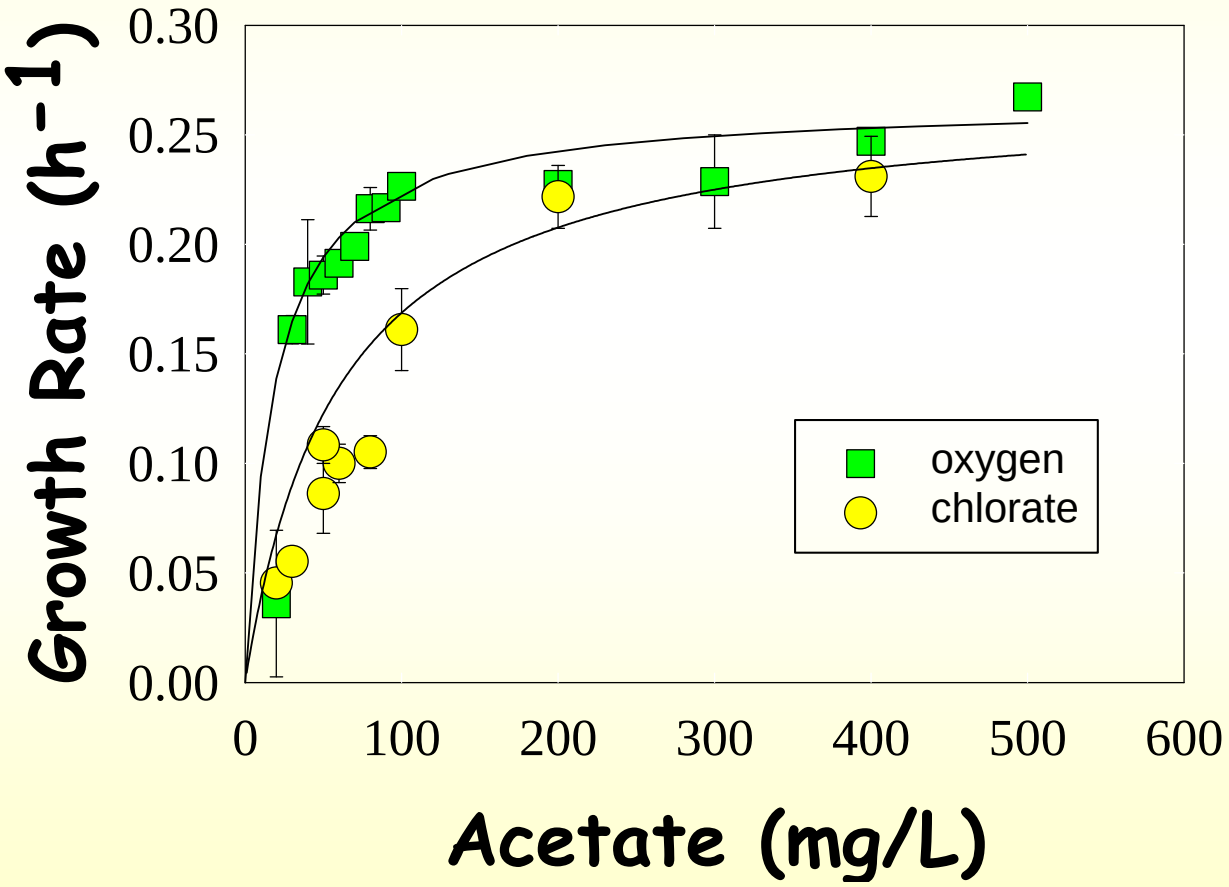

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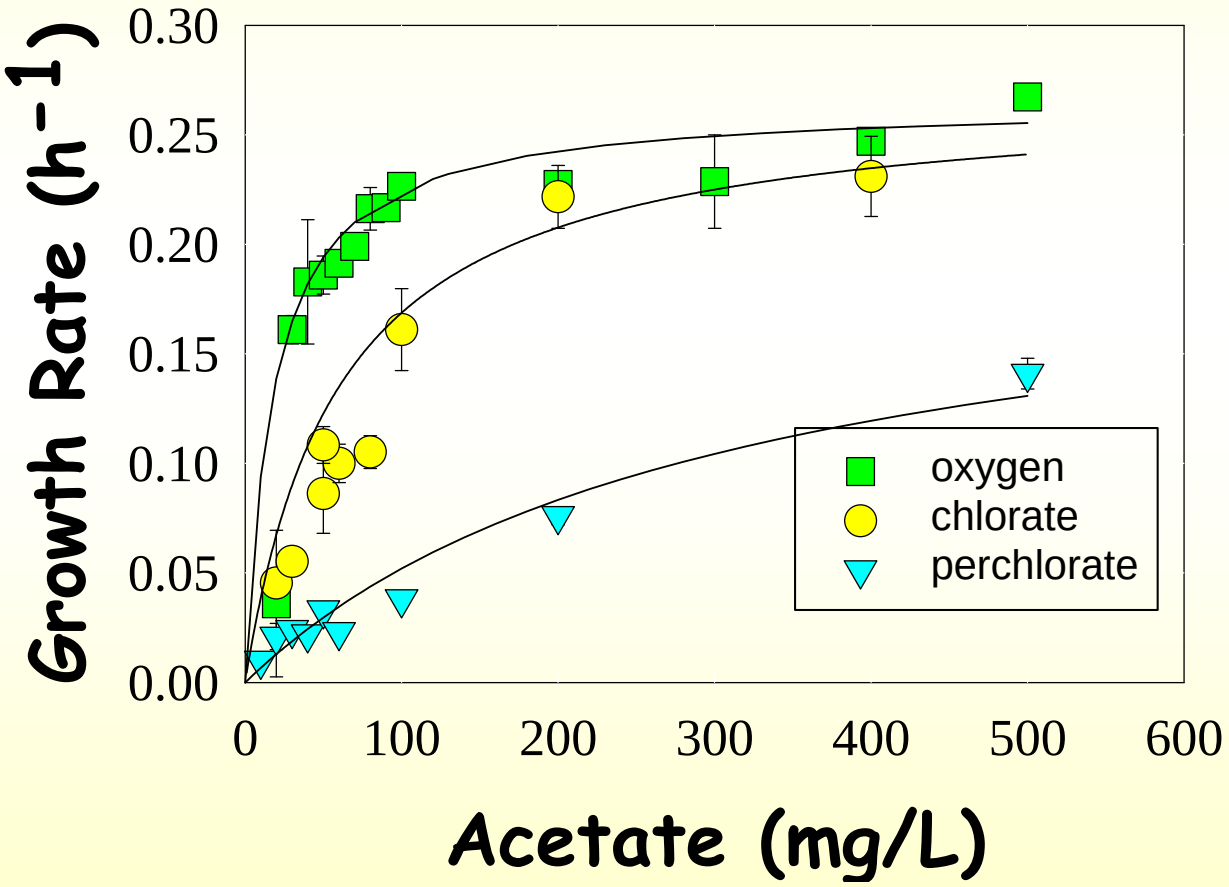


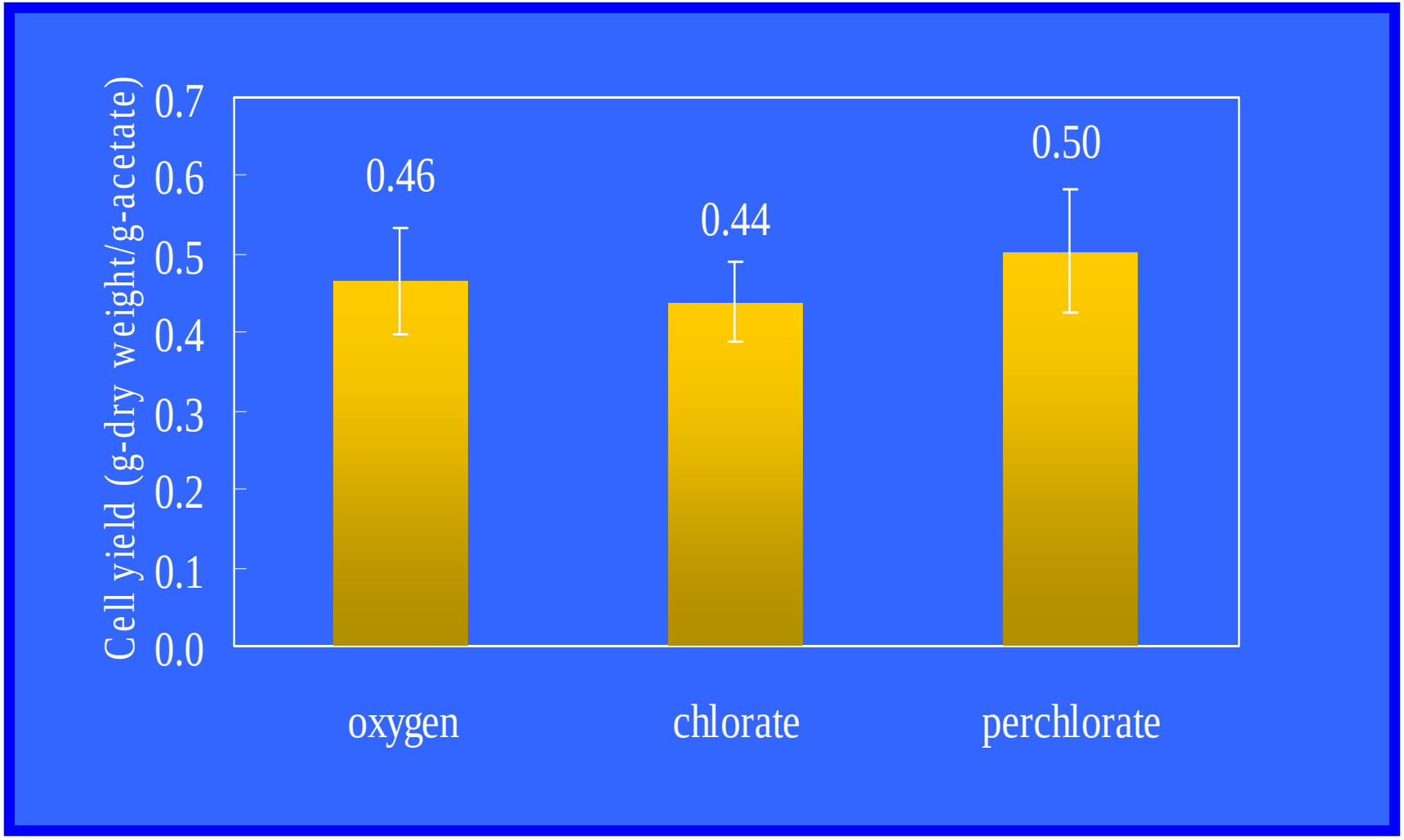
From: Logan et al. (2001)

Kinetic constants for growth of KJ on acetate

Electron Acceptor	**μ_m (h^{-1})**	**K_S (mg/L)**
Oxygen	0.27 ± 0.02	14 ± 1
Chlorate	0.27 ± 0.03	60 ± 25
Perchlorate	0.14 ± 0.01	470 ± 290

From: Logan et al. (2001)

Cell yield- KJ



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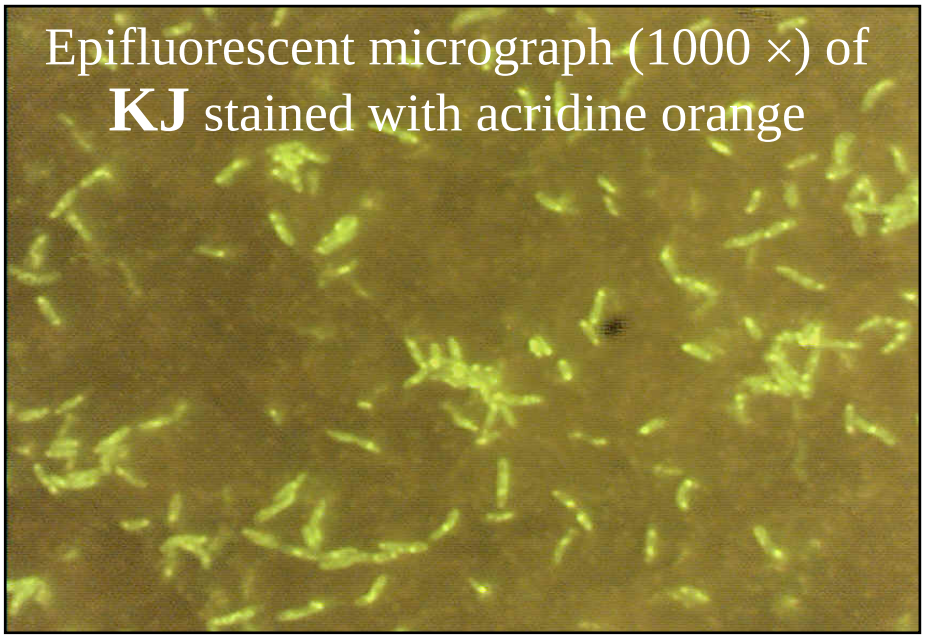
From: Logan et al. (2001)

Overall Stoichiometry



Without biosynthesis: acetate/perchlorate = 1:1 (mol/mol)

$$CH_3COO^- + ClO_4^- \rightarrow 2HCO_3^- + H^+ + Cl^-$$

With biosynthesis: acetate/perchlorate = 2.9:1 (mol/mol)

$$CH_3COO^- + 0.35ClO_4^- + 0.26NH_4^+ + 0.04H^+ \rightarrow$$

$$0.26C_5H_7O_2N\ (cells) + 0.7HCO_3^- + 0.35Cl^- + 0.78H_2O$$

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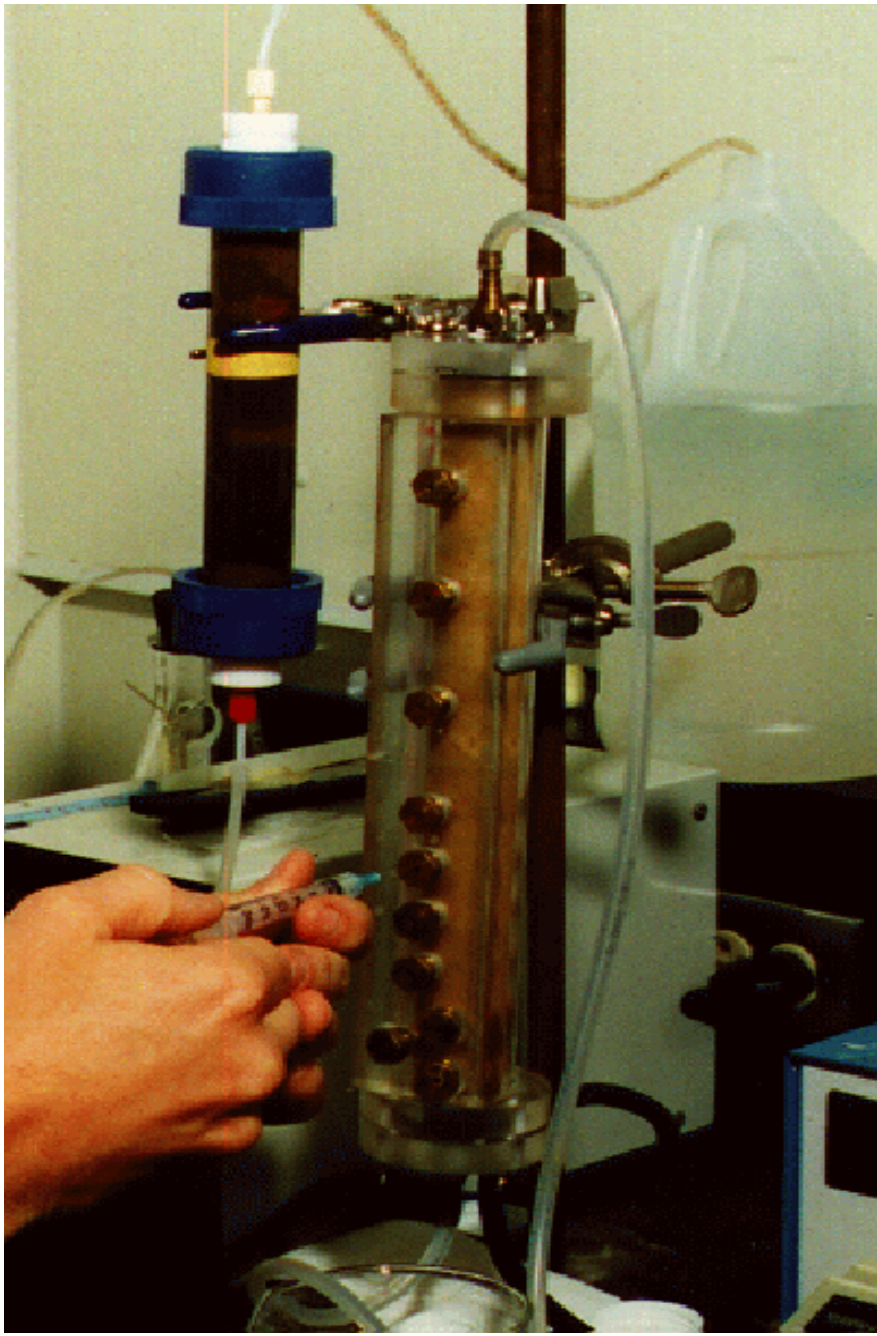
Acetate-Fed Sand Packed-bed Column Experiments

Sampling from the side ports of the column



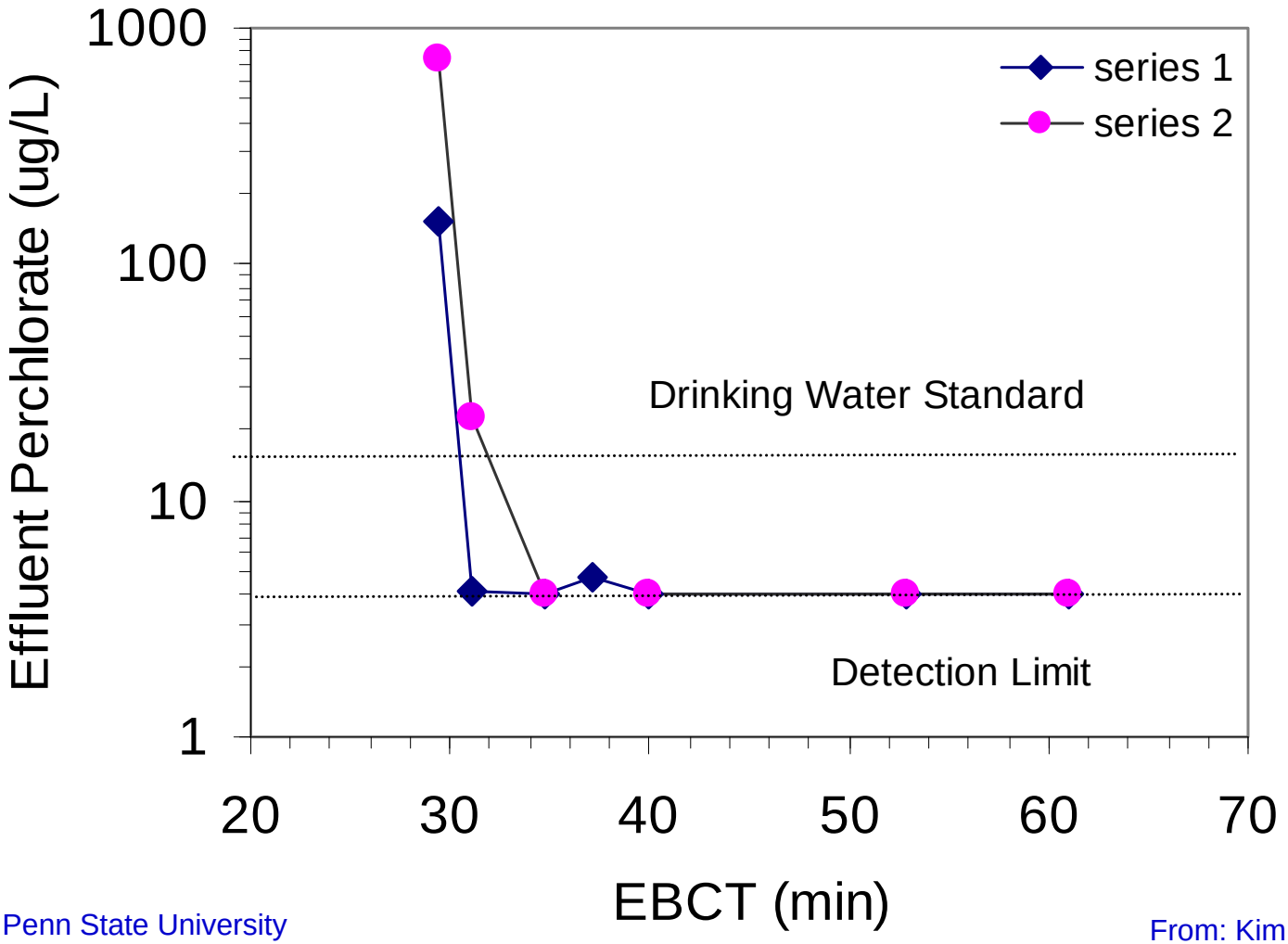
Acetate-fed Bioreactors

- **Columns:** 14 cm or 28 cm long.
- **Mixed cultures:** enriched on perchlorate (activated sludge samples)
- **Pure culture:** *Dechlorosoma* sp. KJ
- **Feed:** Artificial groundwater (AGW) containing 20 mg/L perchlorate and nutrients; water from the City of Redlands

Mixed cultures

(14 cm sand column)

Critical EBCT was 34 minutes.



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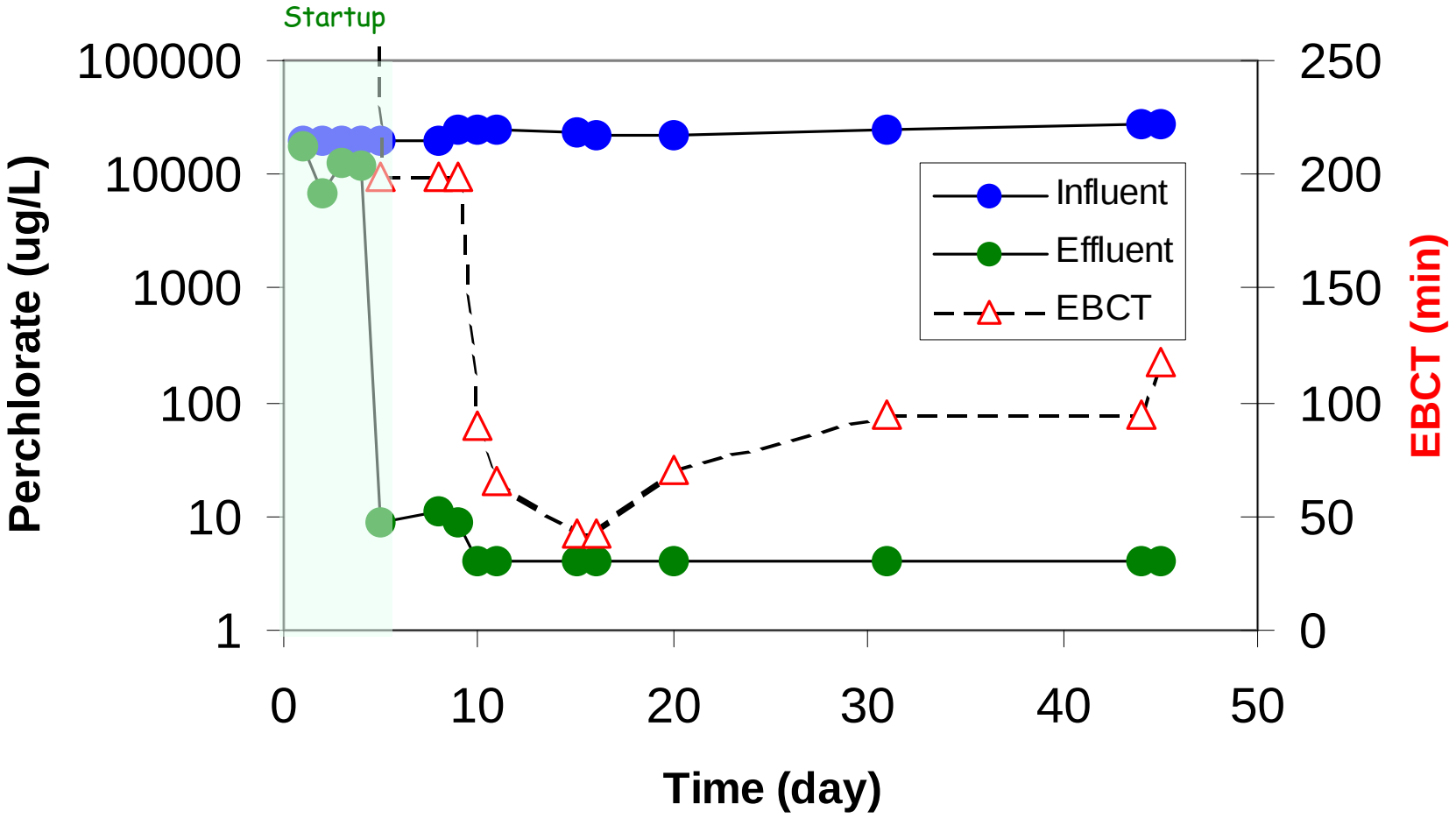
From: Kim and Logan (2000)

Mixed cultures

(28 cm sand column)

Critical EBCT was ~40 minutes.

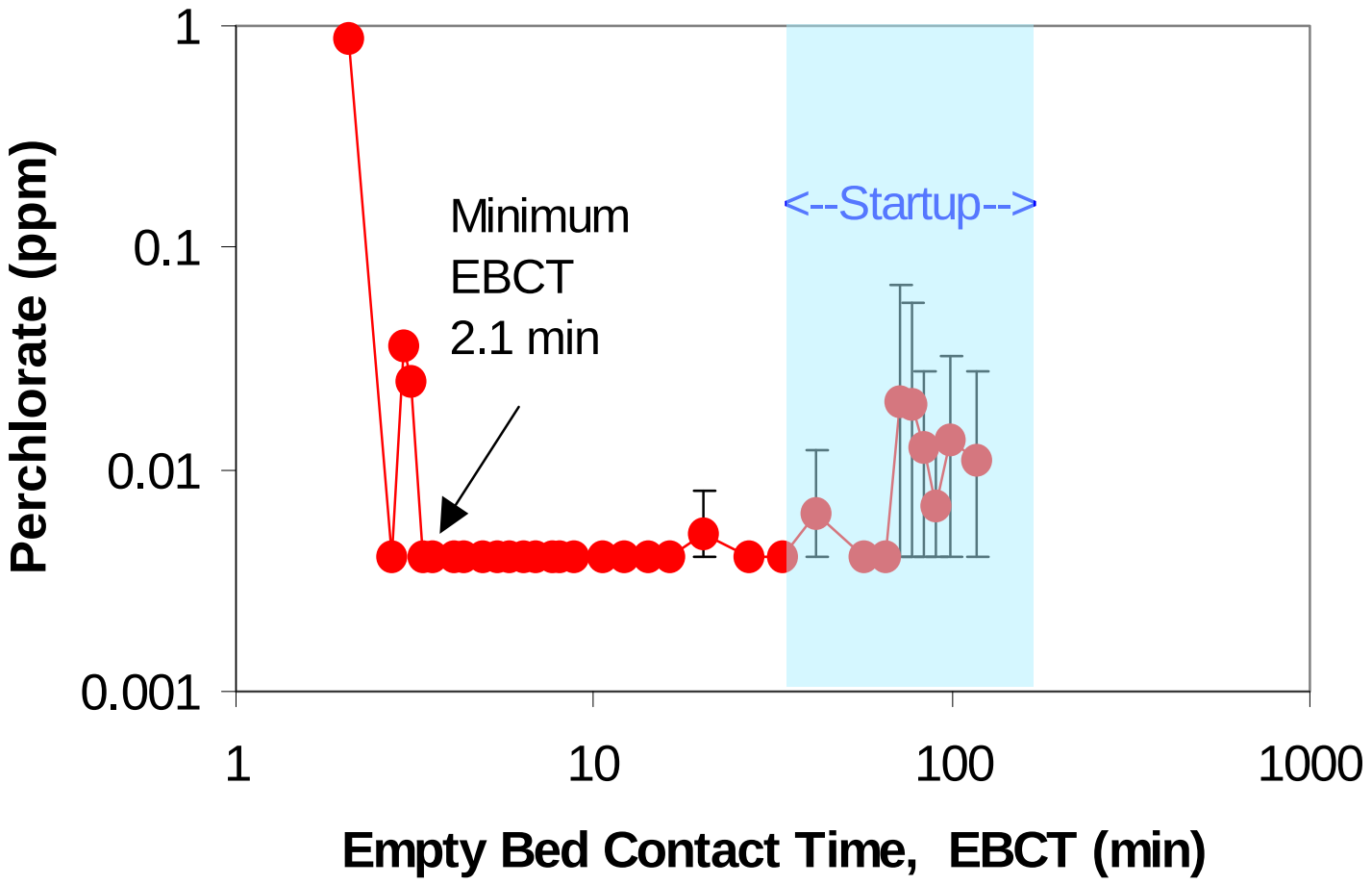


From: Kim and Logan (2000)

Pure culture: KJ

(28 cm-sand column)

Critical EBCT was ~2.1 minutes.



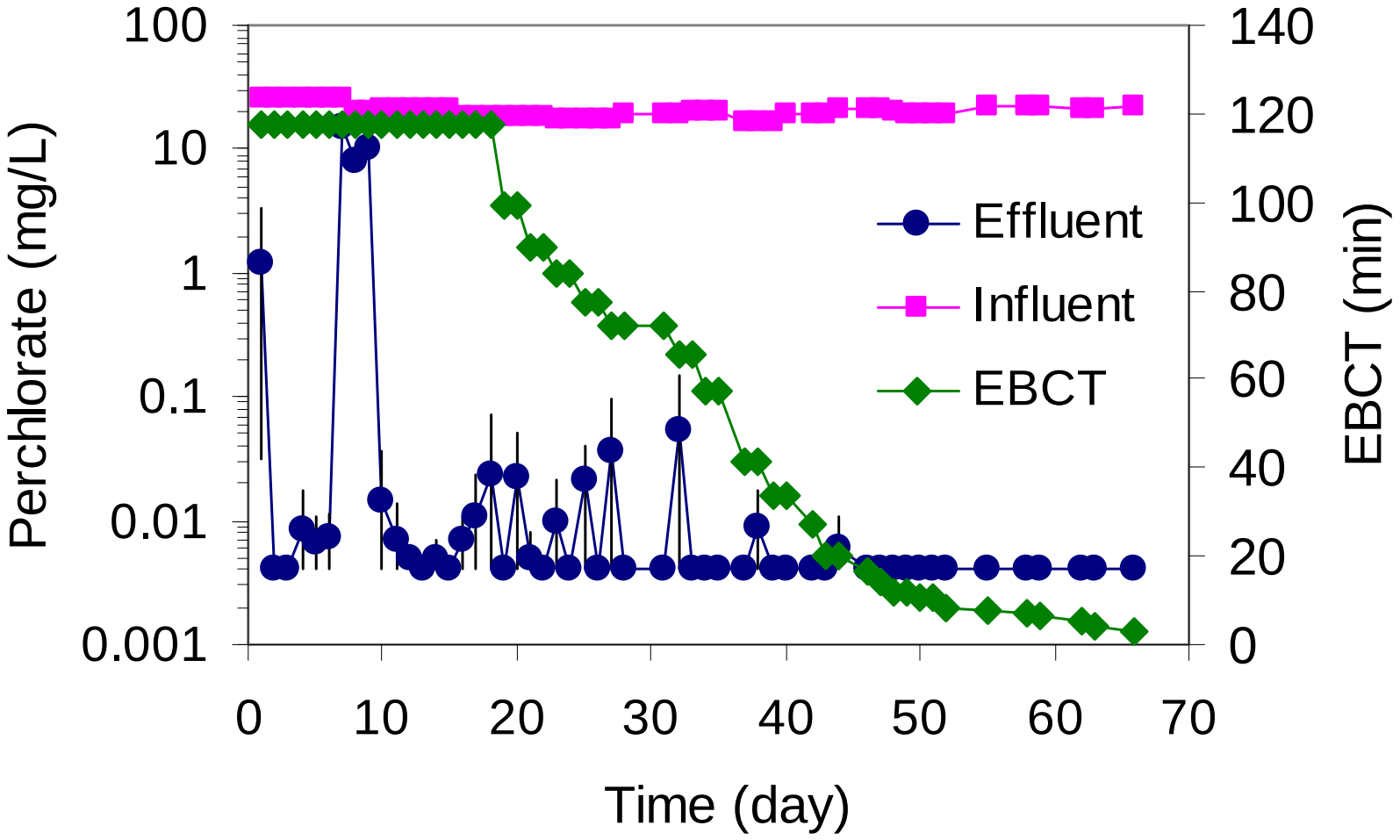
From: Kim and Logan (2001)

Pure culture: KJ

(28 cm-sand column)

As EBCT decreased:

Perchlorate was non-detectable for 84% of samples (n=147)



From: Kim and Logan (2001)

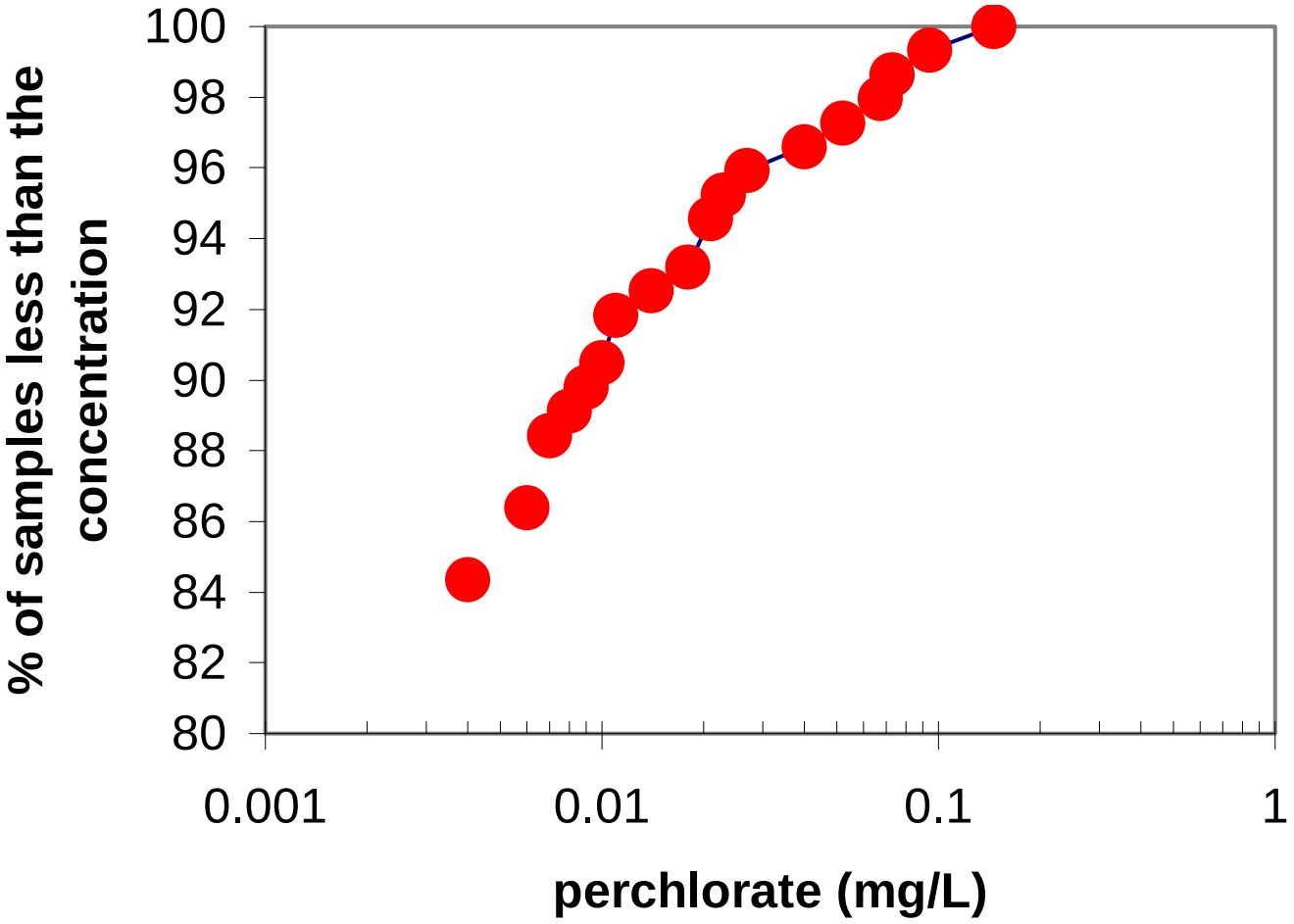
Pure culture: KJ

(28 cm-sand column)

Reliability: After start up, perchlorate removal was stable at:

95% of time: <23 ppb

84% of time: <4 ppb

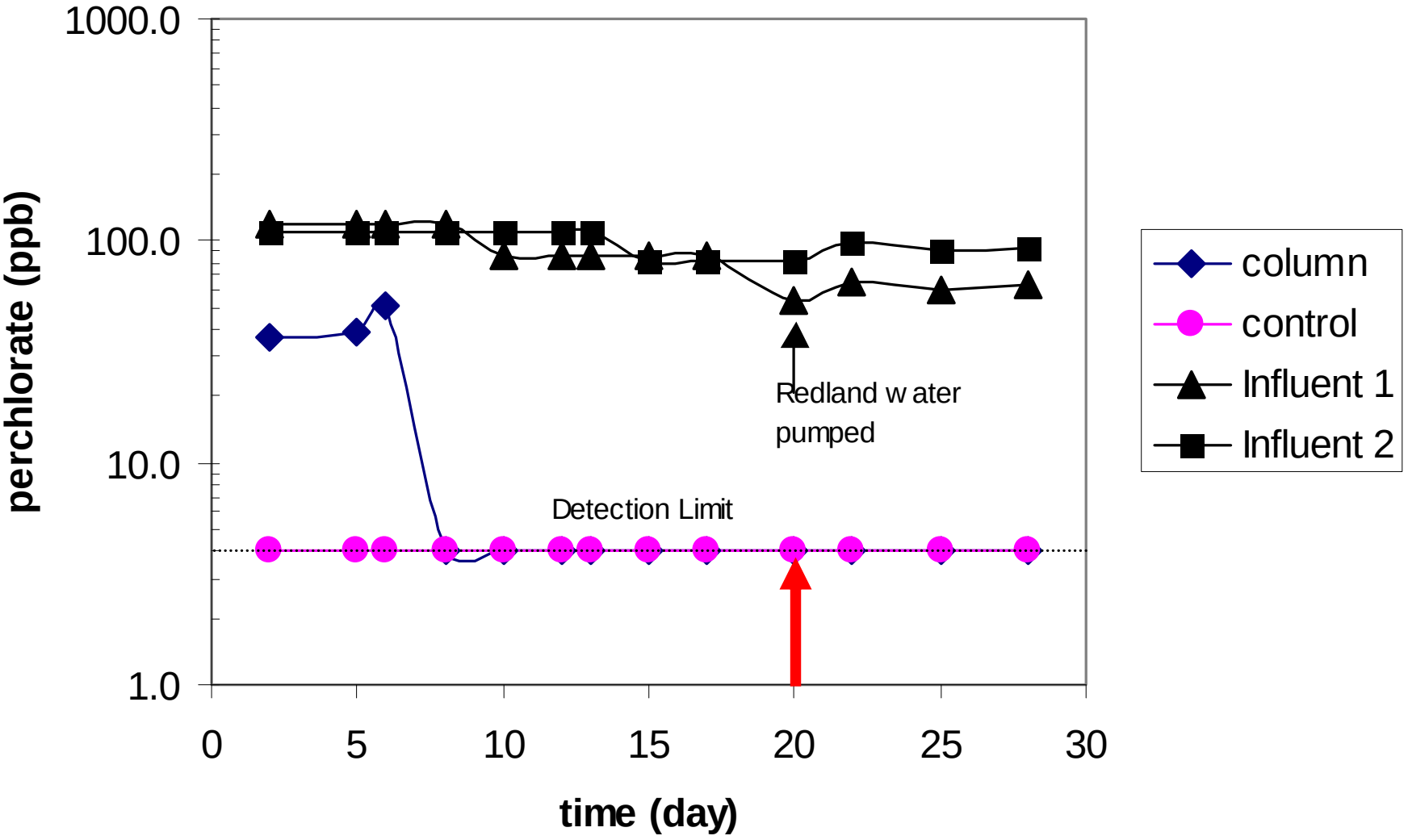


From: Kim and Logan (2001)

Redlands Water

Pure culture KJ, (28 cm-sand column)

Perchlorate is completely removed using groundwater from Redlands site.



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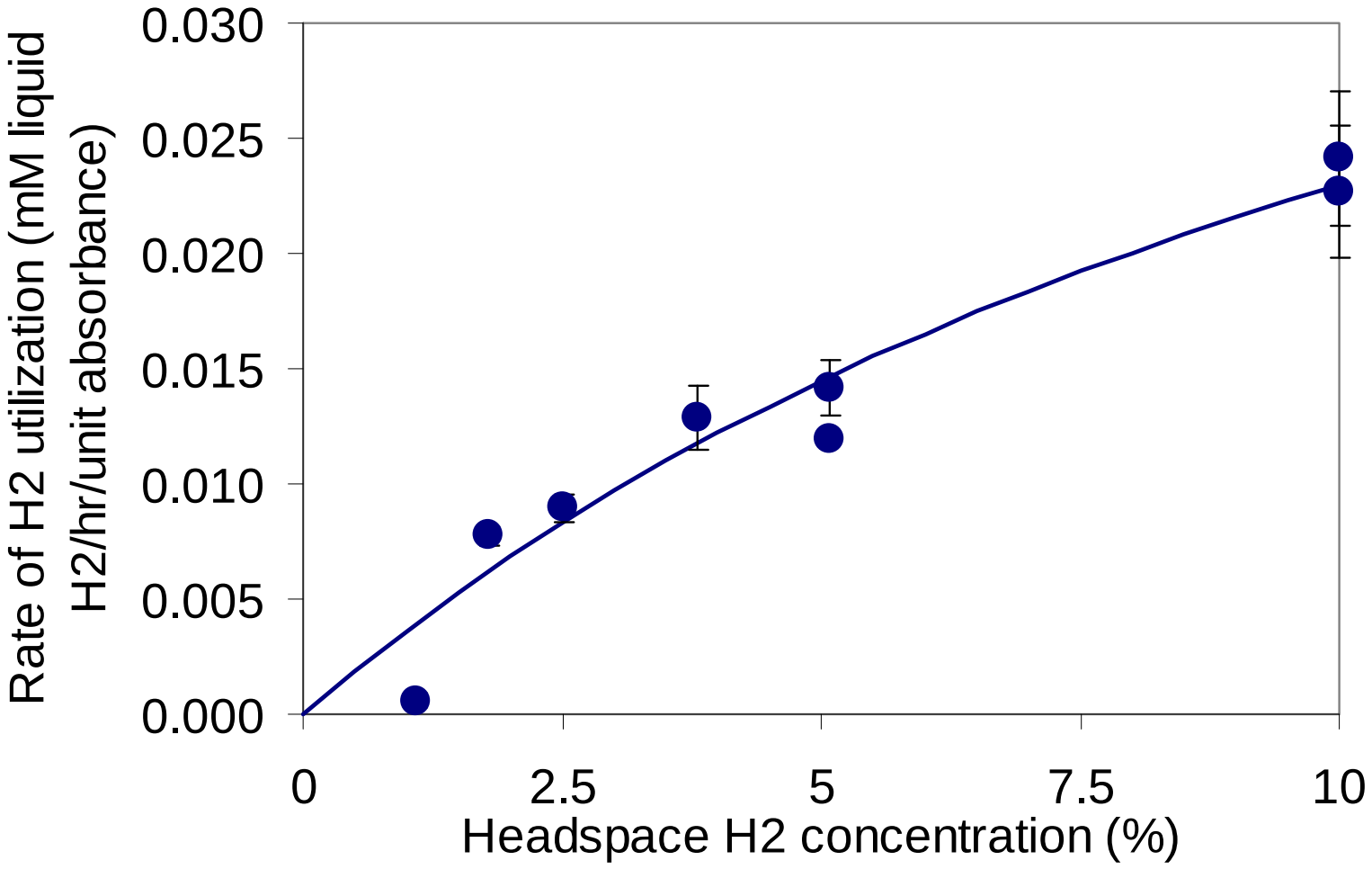
Perchlorate reduction supported by Hydrogen gas

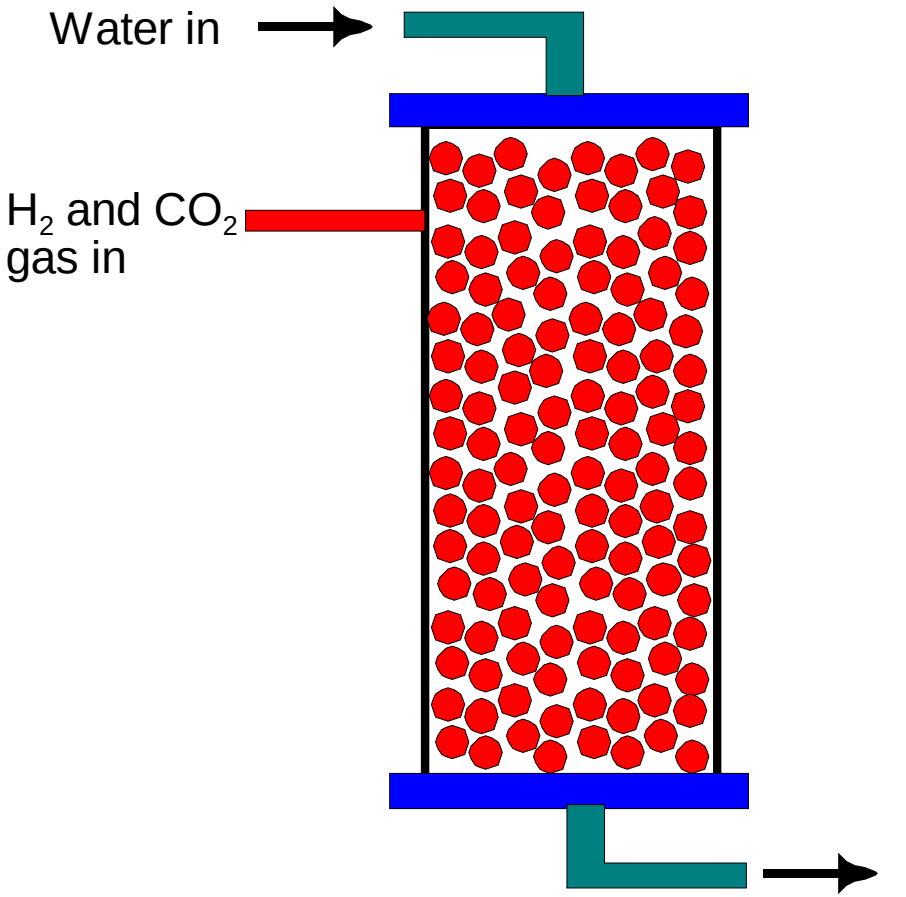


From: Miller and Logan (2000)

Hydrogen Reactor

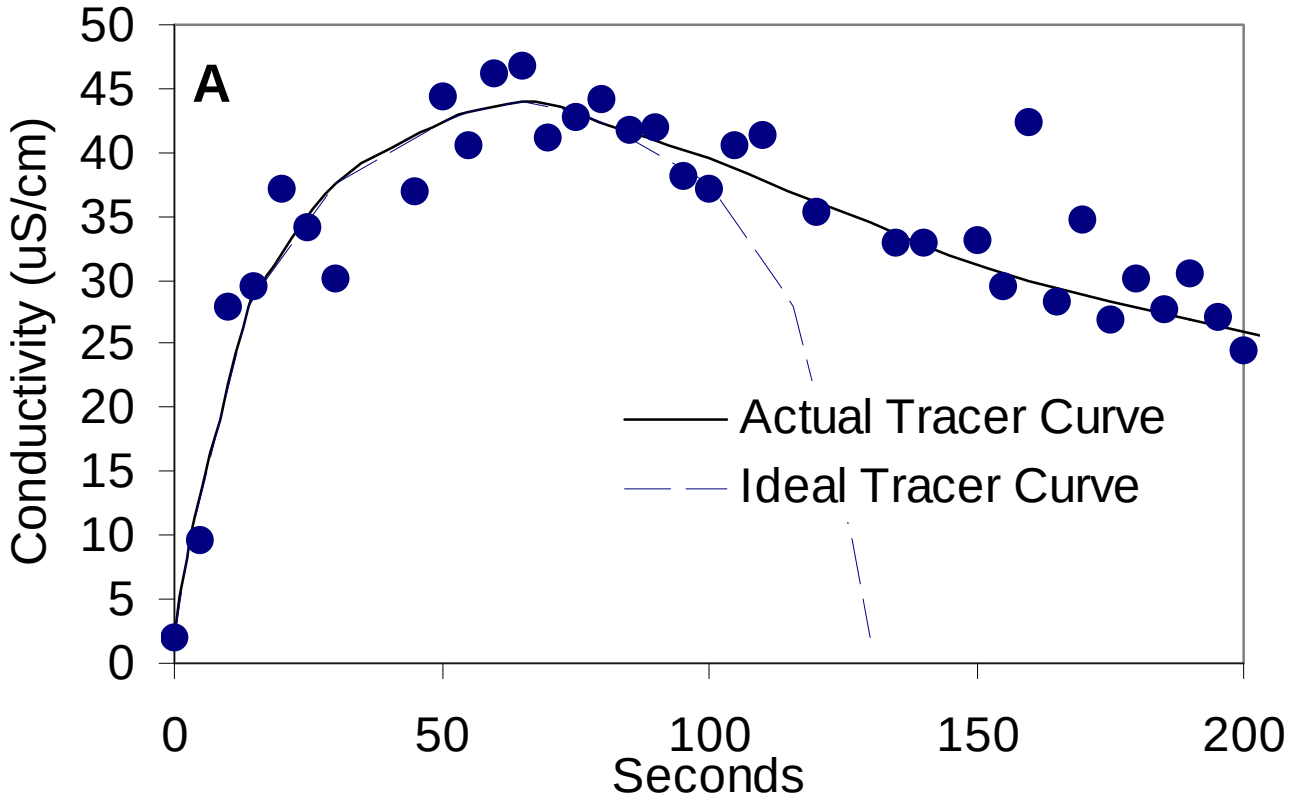
- **Column:** 12.5 cm (10 mm packed), 2.5 cm diameter
- **Packing:** 3 mm diameter glass beads (1200 m^2/ m^3)
- **Pumping Solution:** 740 μg/L perchlorate in trace metal solution
- **Gas mixture:** H_2, 43 mL/min and CO_2, 7.5 mL/min)
- **Operation period**: 145 days

Fixed film biohydrogen reactor
(unsaturated flow)



Hydrogen Reactor

Average detention times of 1.0-1.3 minutes

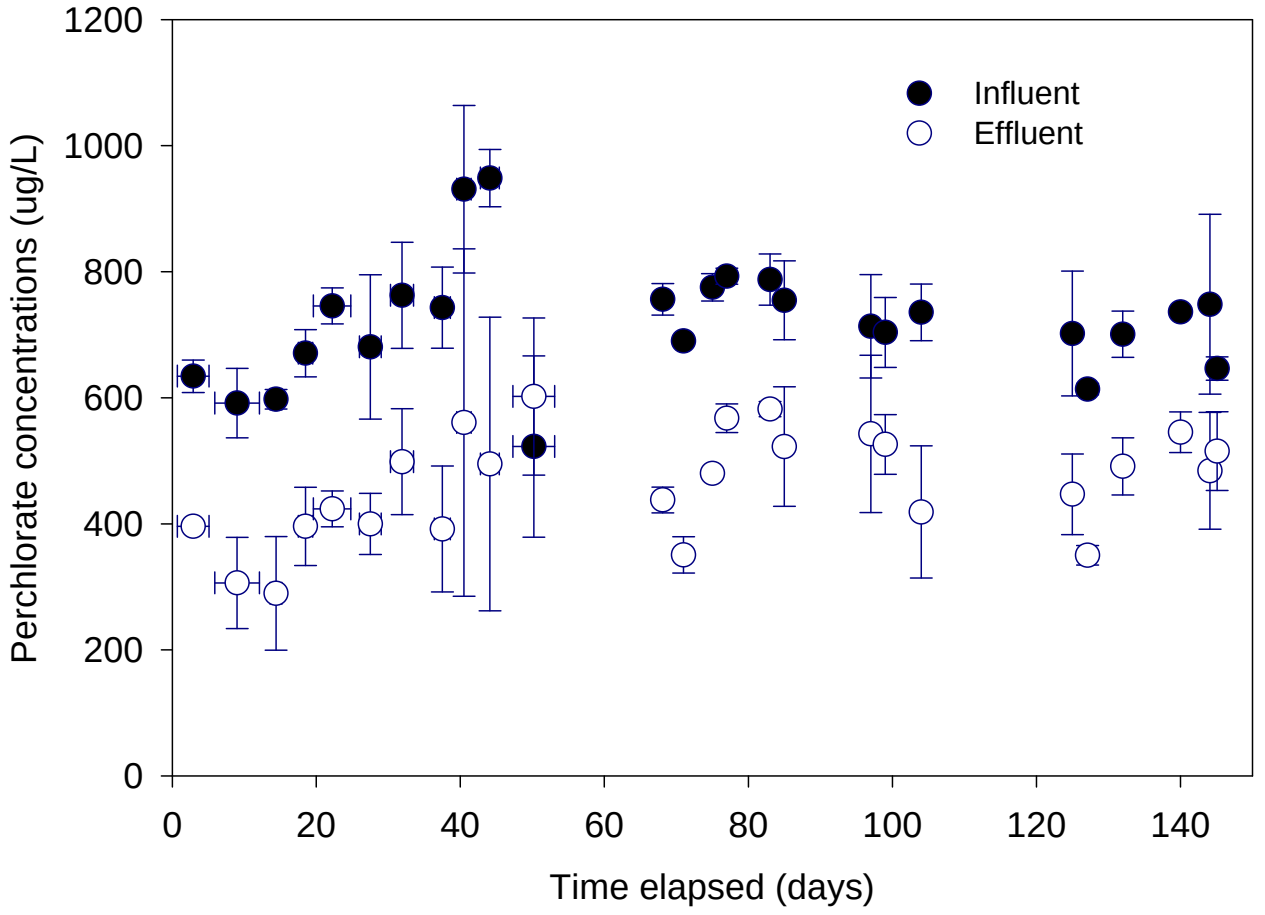


Hydrogen reactor performance

In: 740 ±110 μg/L

Out: 460 ±80 μg/L

Removal: **38%** ±9%



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Reactor Kinetics: Removal Rates

- Expect removal rate, R, is 1st-order with respect to perchlorate concentration.
- Rate calculated as:

$$R = \frac{(Cin - Cout)}{\theta}$$

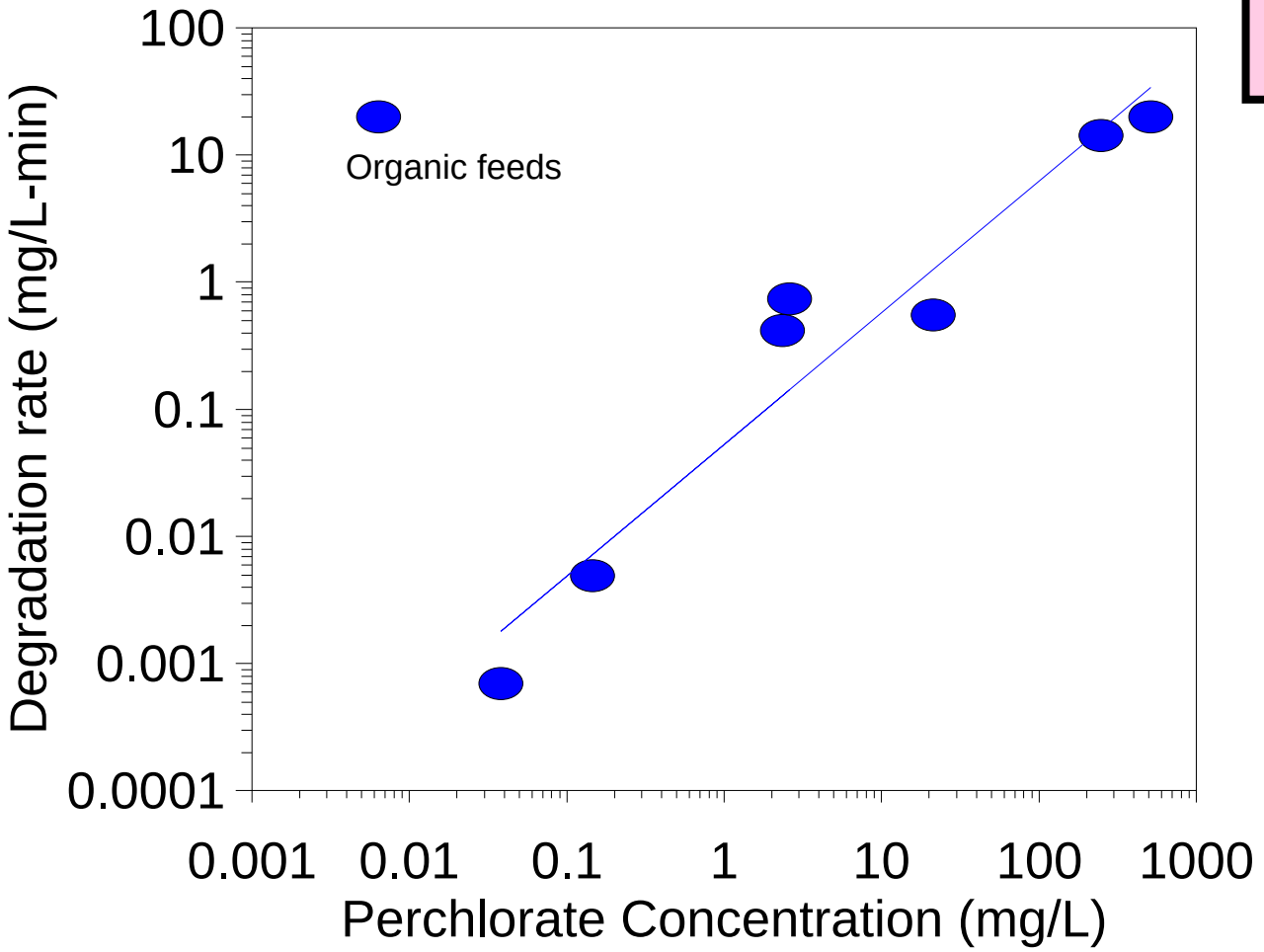
- For 1st-order kinetics, use log mean perchlorate concentration

$$C_{lm} = \frac{C_{in} - C_{out}}{\ln (C_{in} / C_{out})}$$

Perchlorate Bioreactor Rates

(Data prior to 2001; Mixed cultures, organic substrates)

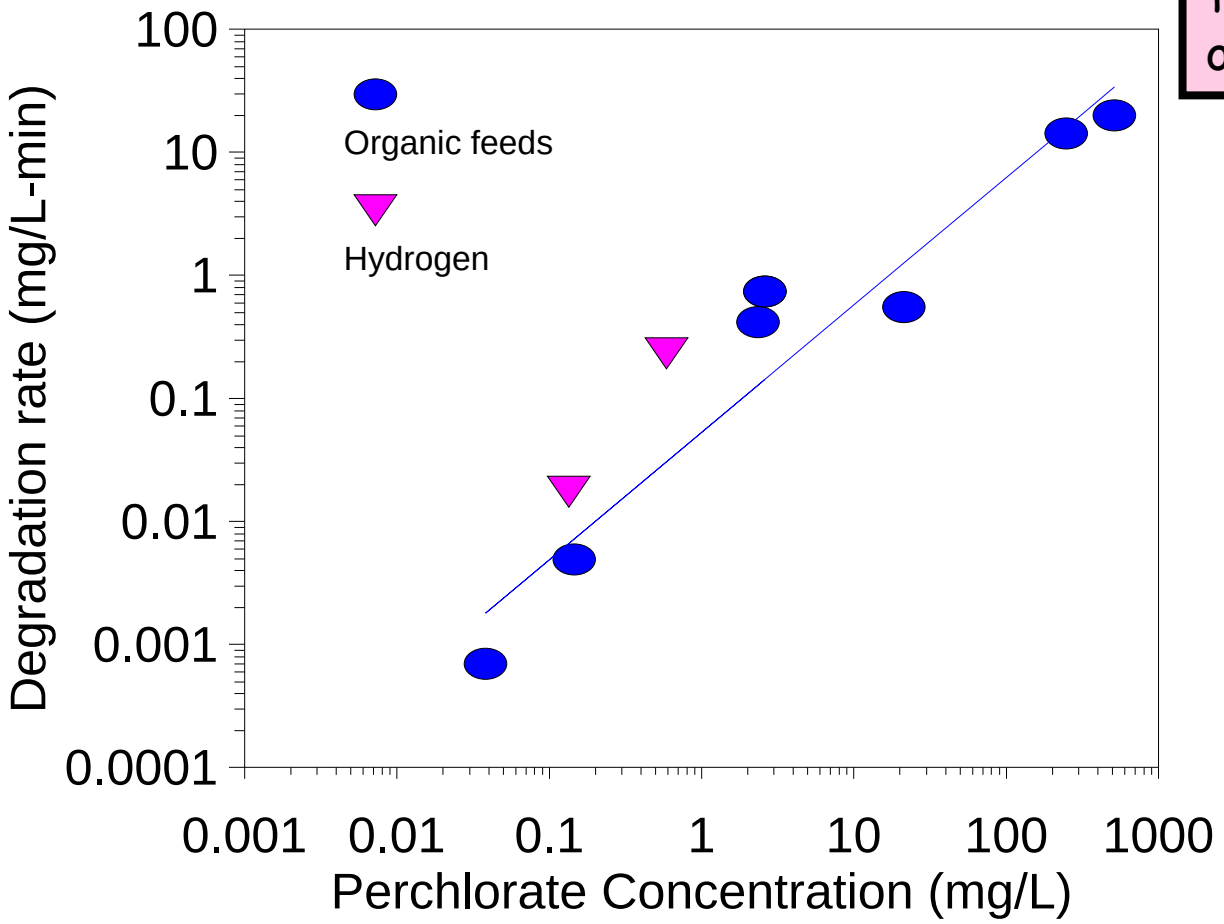
Rate indicates first order kinetics with concentration



From: Logan (2001)

HYDROGEN REACTOR

H_2 reactor rates are slightly higher than those in other types of reactors



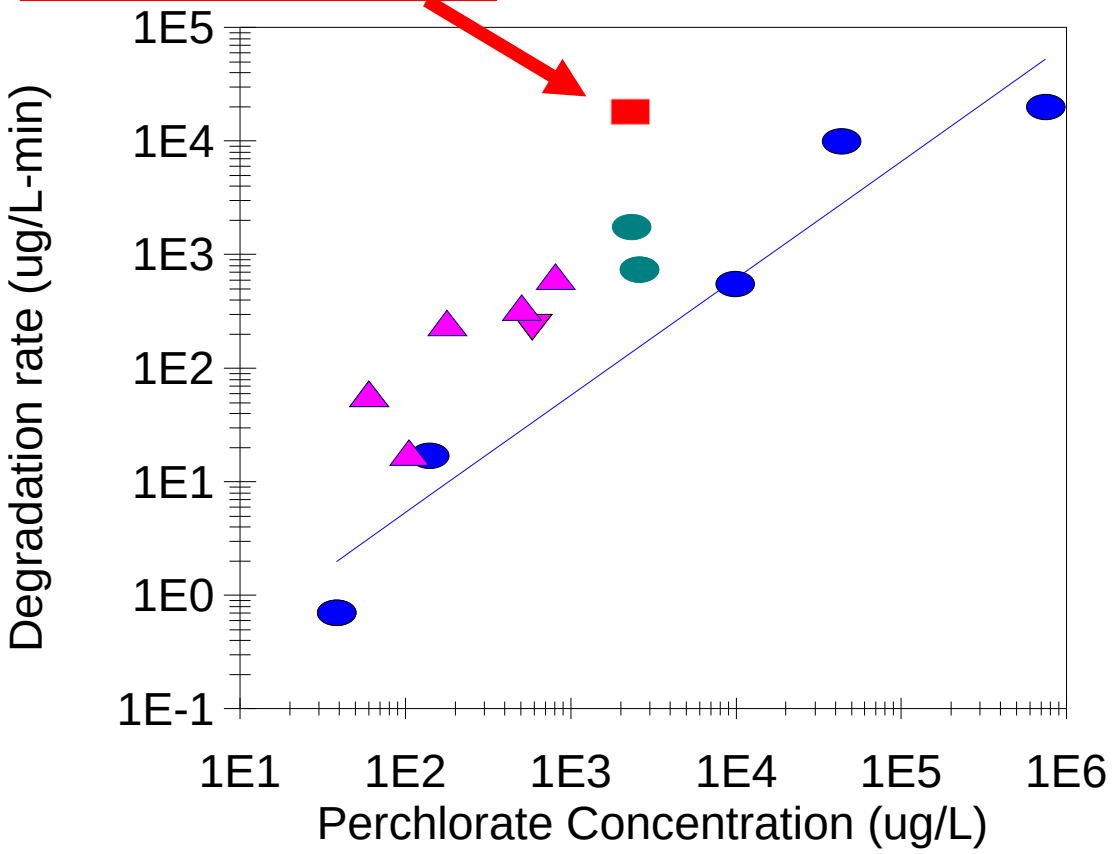
From: Logan (2001)

ALL PERCHLORATE BIOREACTOR REMOVAL RATE DATA

(Sand Column Reactor Data)

Pure culture (KJ) reactor

The pure culture rate is an order-of-magnitude greater than other rates at comparable perchlorate concentrations



Previous — Organic substrates; non-PSU studies

H2

H2 — All hydrogen reactor data (some is unpublished)

PSU- KJ

PSU- Mixed — PSU= Penn State Reactors

Adapted from Logan (2001)

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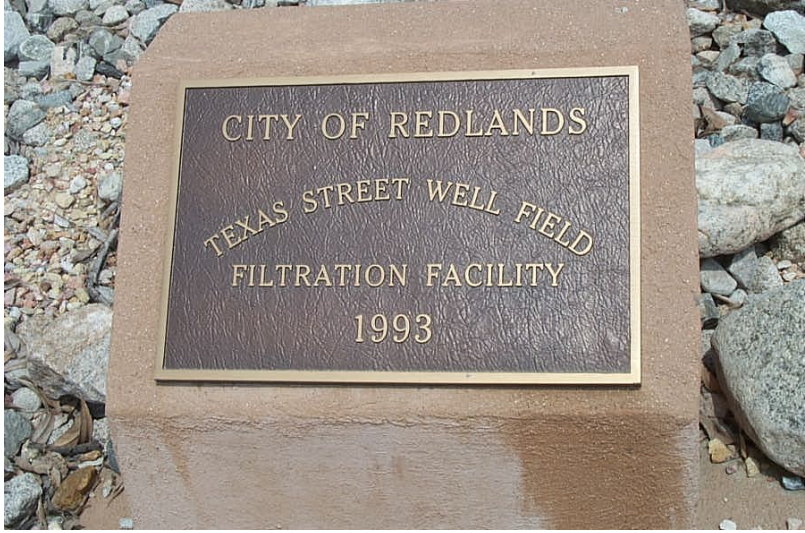
Study Participants



- Site: Redlands, California, Texas St well field
- Engineering Firm: Camp, Dresser and McKee
- Research Unit: The Pennsylvania State University
- Funding Agency: American Water Works Association Research Foundation (AWWARF; via an EPA Grant)

Study site: City of Redlands

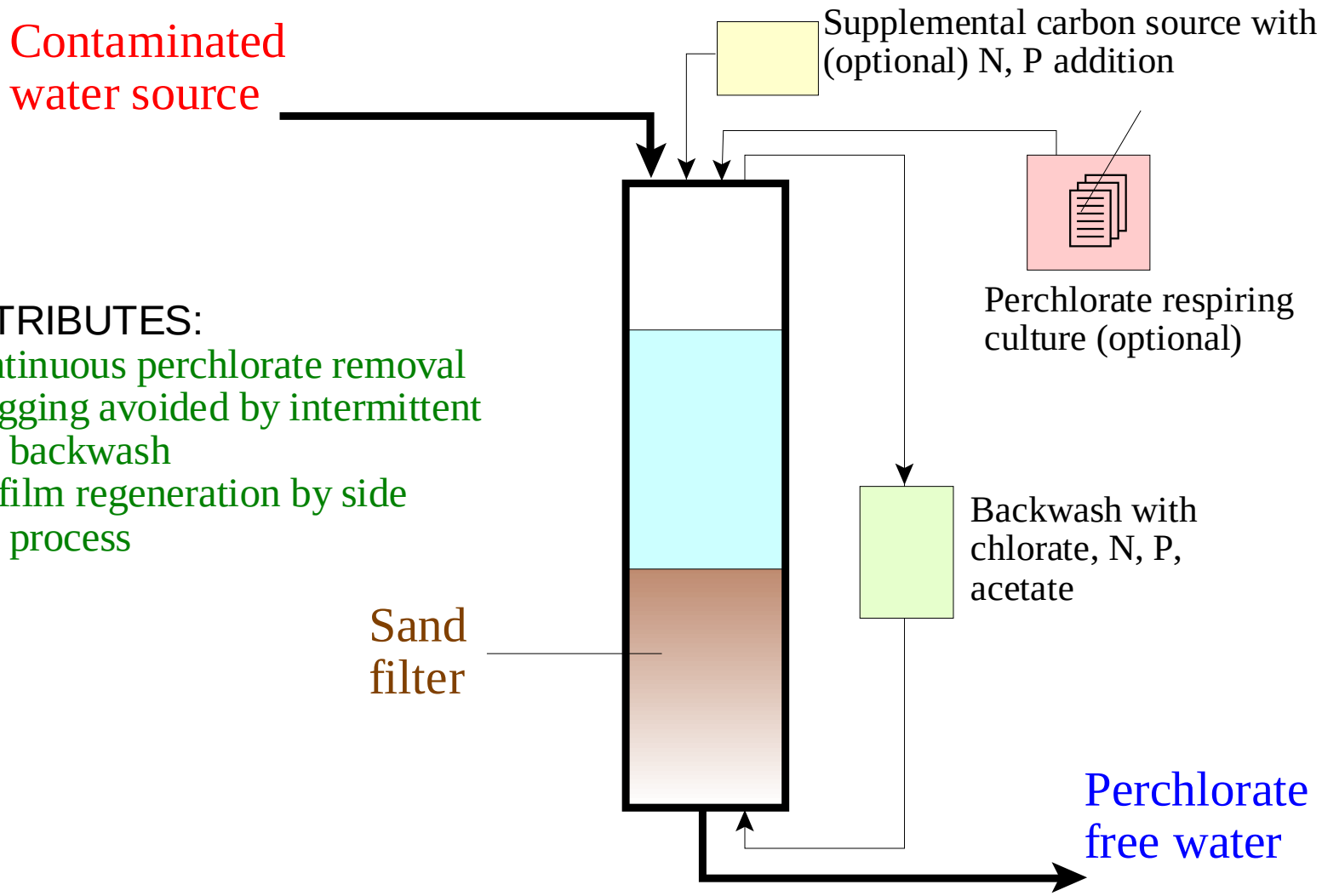
Map from the University of Redlands website

Texas St. Site in Redlands has 24 GAC columns (shut down due to perchlorate breakthrough)

B. Logan, Penn State University

PERCHLORATE FIXED-BED BIOREACTOR

Patent No. 6214607



ATTRIBUTES:

Continuous perchlorate removal

Clogging avoided by intermittent backwash

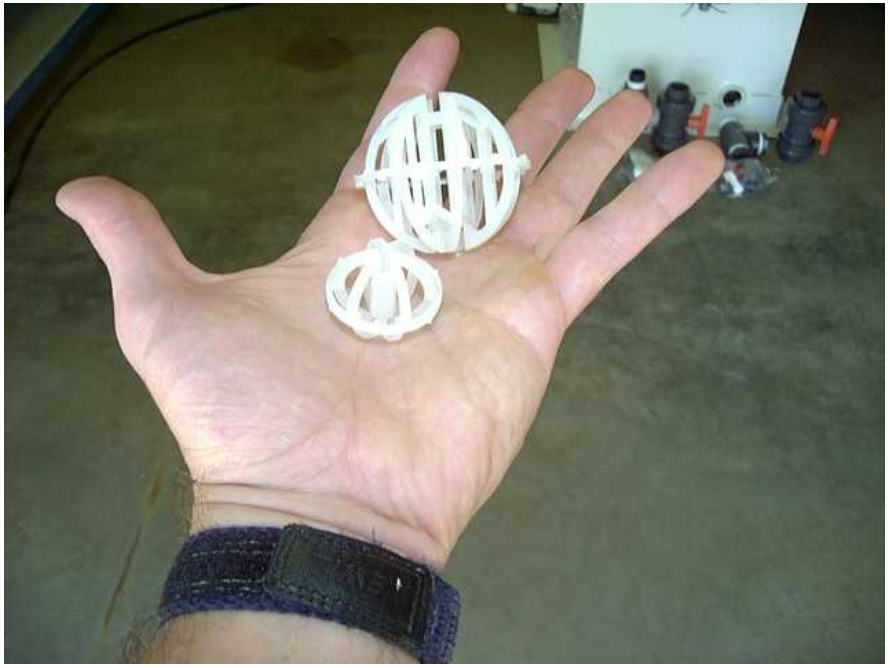
Biofilm regeneration by side process

Pilot plant Specifications

- Feed: groundwater, acetic acid, ammonium phosphate
- Two bioreactors in parallel:
  - Sand
  - Plastic media
- Monitoring:
  - flow, pressure, pH, dissolved oxygen,
  - Perchlorate, acetate, nitrate

Media Used in Two Reactors operated in parallel

Tri-Pack Plastic Media



Sand (1 mm diameter)

Raw water supply- Redlands Site

Bioreactors housed on site in a converted garage (Redlands, CA)

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Filter inlet controls

B. Logan, Penn State University

In line mixers, flow measurement, and flow controller

B. Logan, Penn State University

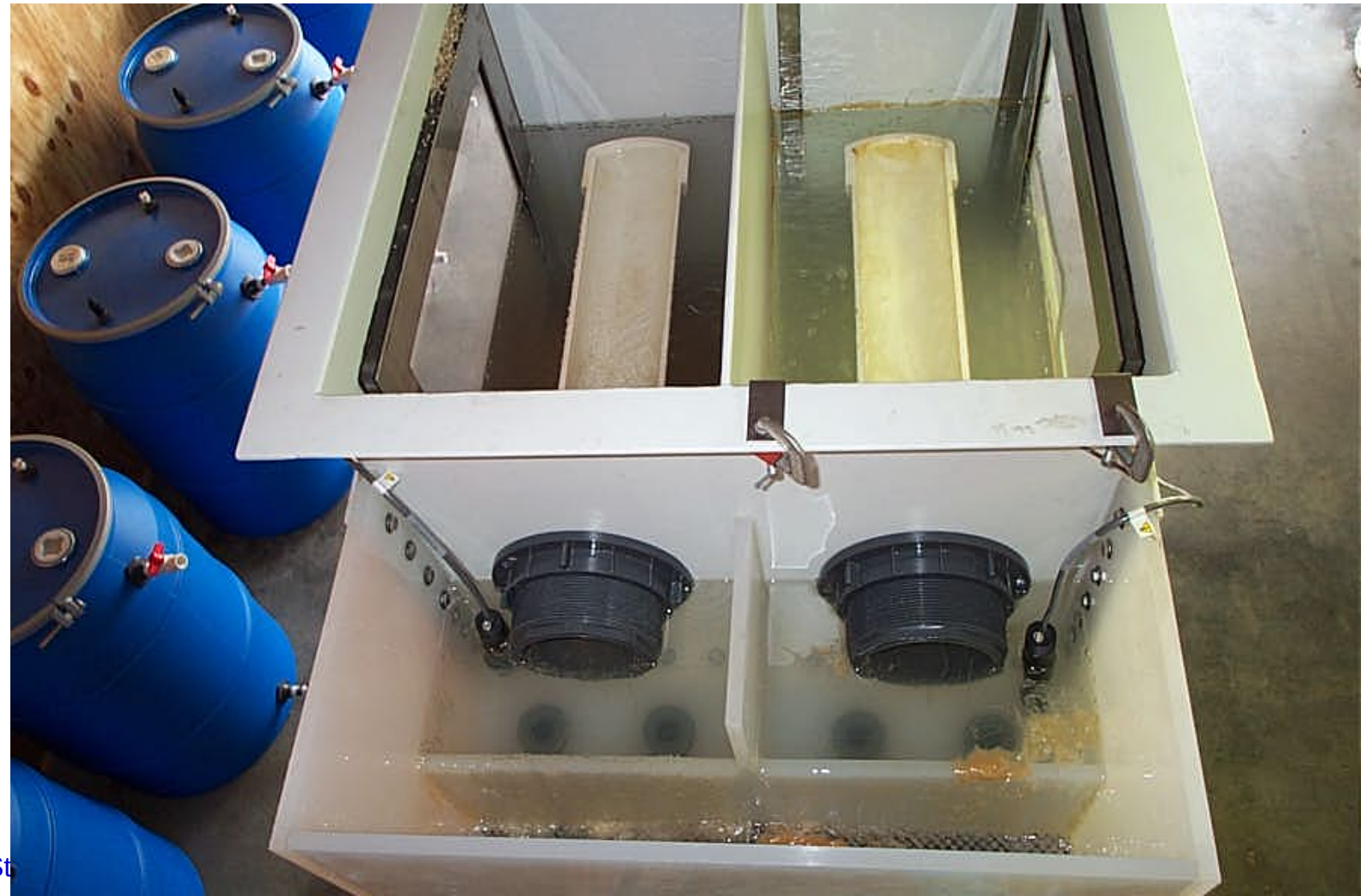
Filter pumps, one for each reactor

B. Logan, Penn State University

Sand media reactor

Plastic media reactor

Water exits at reactor top (via an overflow weir) to a drain

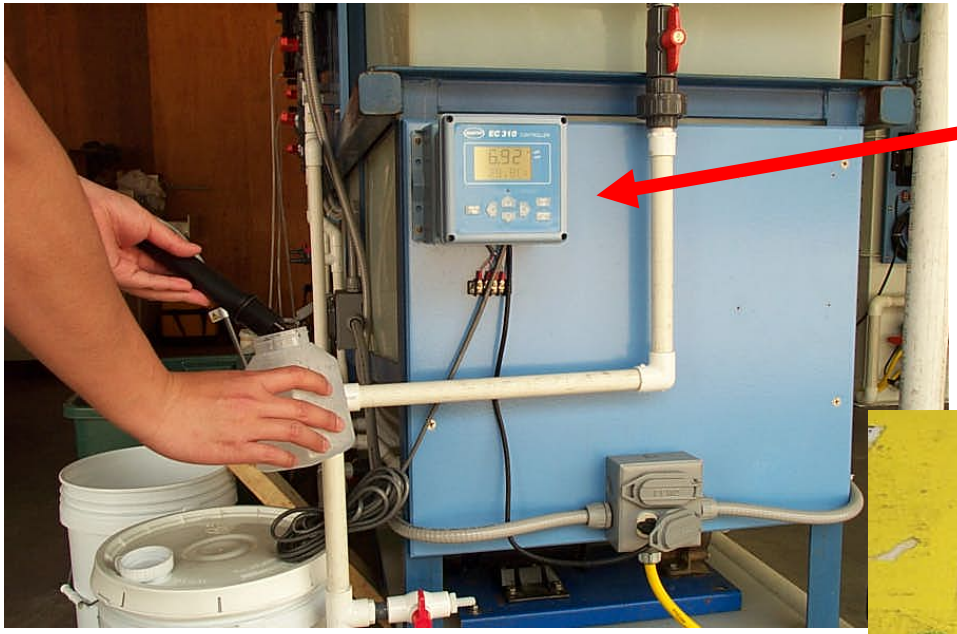


Water then goes to a holding tank that is periodically emptied

Water quality monitoring panel

B. Logan, Penn State University

Monitoring water quality



Influent pH after acetate addition

Dissolved oxygen, pH, and conductivity at any location

Samples can be obtained along each reactor

The reactors can be backwashed and air scour used to mix media

B. Logan, Penn State University

Preliminary Pilot Plant Results

- Two bioreactors are just in startup phase (running about 2 weeks)
- Flow is 1 gpm/reactor
  - Sand column: 20 min detention time
  - Plastic media: 60 min detention time
- During this startup phase, perchlorate was reduced from 70 ppb to:
  - Sand column: 10 ppb initially, <4 ppb after first backwashing
  - Plastic media: 40 ppb initially, <4 ppb after first backwashing

Preliminary Pilot Plant Results

- Dissolved oxygen: completely removed
- Effluent pH: 6.7 – 6.9
- Turbidity: 2-4 NTU
- Nitrate: evidence of gas bubbles
- Odors: none during operation

CONCLUSIONS

- Perchlorate reducing microbes are present in natural water and soil samples, but enriched in perchlorate-contaminated soils.

- It is possible to obtain high perchlorate removal rates, at low EBCT of 2.1 min, in packed bed reactors inoculated with pure culture (KJ)

CONCLUSIONS... continued

- Perchlorate removal was achieved in the laboratory using groundwater from the Redlands site, containing dissolved oxygen and nitrate.

- Pilot scale tests are underway in Redlands California to demonstrate the reliability of perchlorate removal using a large scale reactor and actual groundwater sample.

ACKNOWLEDGMENTS

City of Redlands	Doug Hedricks, Dave Commons, Ken Pang
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Students	Booki Min, Kijung Kim, Yanguang Song, Husen Zhang, Joel Miller
Collaborators	Richard Unz (Penn State), Jaci Batista (UNLV), Robert Arnold (Univ. Arizona)

QUESTIONS ?

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Web page: www.engr.psu.edu/ce/enve/logan.htm

Publications page: www.engr.psu.edu/ce/enve/journal-pubs.htm

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