# Removal of Organic Contaminants from Polyethylene Drinking Water Pipes by Flushing

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*HSRP WEBINAR*

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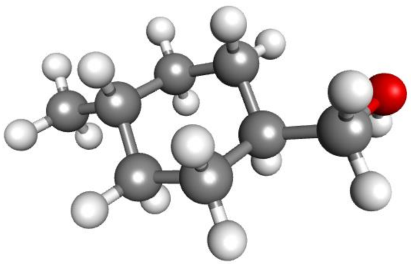
# Flushing for Incident Response

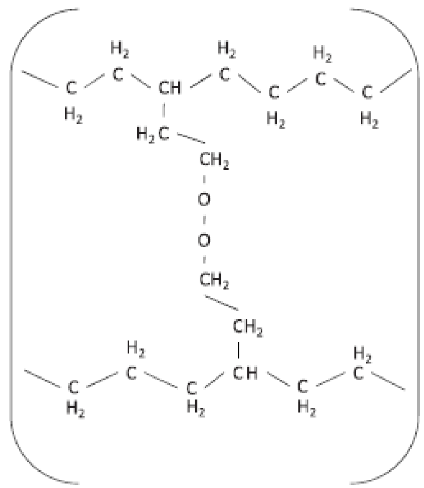
- Charleston, WV, 2014
  - 4-Methylcyclohexanemethanol
  - 300,000 affected
- Utility recommendation: Flush hot water 15 min, cold water 5 min, and appliances 5 min
- Some users reported lingering contamination
  - Water heaters?
  - Permeation into pipes/gaskets?



Casteloes, K. S., R. H. Brazeau, and A. J. Whelton. *Environmental Science: Water Research & Technology* 1.6 **2015**: 787-799.

# Plastic Pipes

- Advantages
  - Light
  - Flexible
  - Inexpensive
- Uptake and release of organic contaminants are expected to become increasingly important for decontamination of plumbing systems.

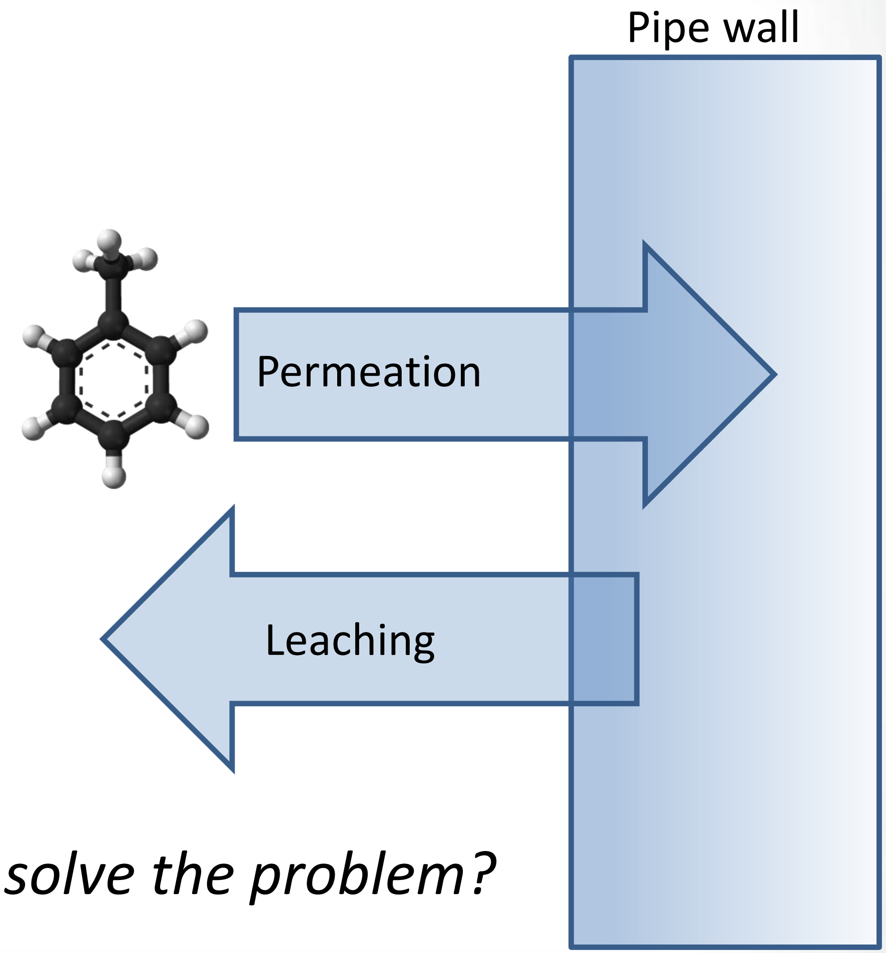


Kelley, K.M.; Stenson, A.C.; Dey, R.; Whelton, A.J. *Water Res.* **2014**, *67*, 19–32.

Whelton, A., Dietrich, A., and Gallagher, D. *J. Environ. Eng.*, **2010,** 10.1061, 227-237.

# Contamination of Plastic Pipe

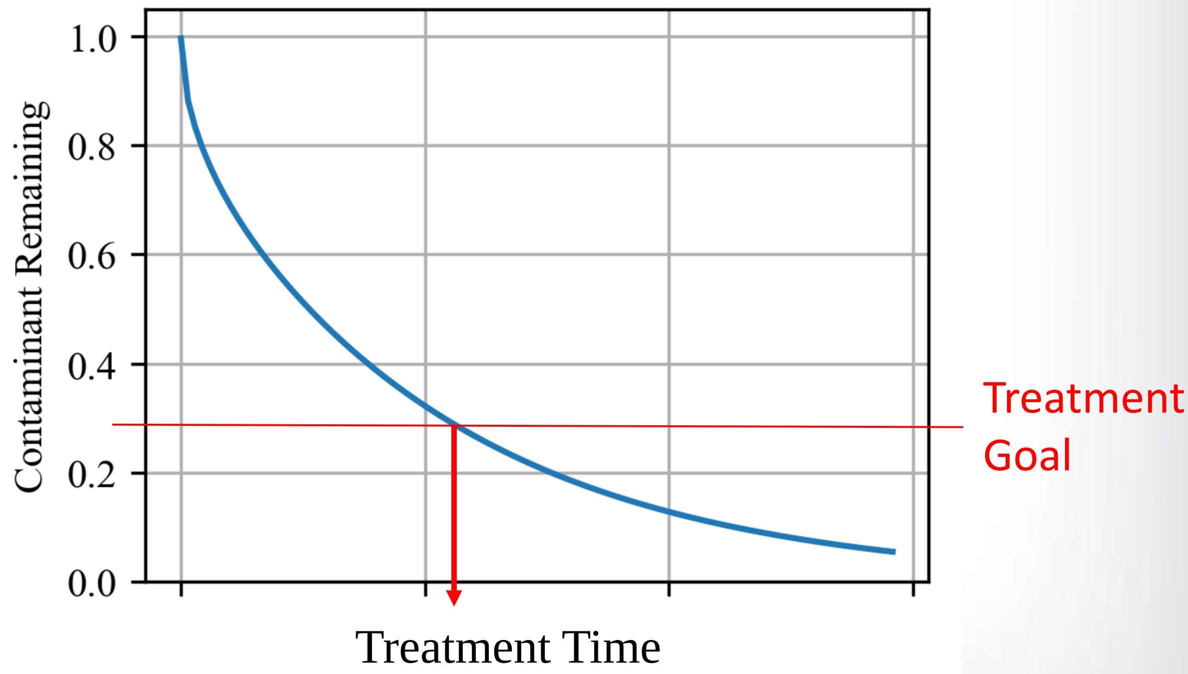
- Contamination of polyethylene pipe is different from metal or concrete lined pipe.
- Some chemical contaminants can infiltrate the bulk of pipe wall.




*Is 30 minutes of flushing enough to solve the problem?*

# *Study Goals*

- Apply diffusion theory to predict required flushing duration
- Determine critical parameters
- Test predictions
- Generalize model



# Diffusion Theory

- Diffusion is governed by a partition coefficient and a diffusion constant, each specific for contaminant/pipe material pair

- Underlying equations aren't easy to apply.

If $M_t$ denotes the quantity of diffusing substance which has entered or left the cylinder in time $t$ and $M_\infty$ the corresponding quantity after infinite time, then

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2\alpha_n^2} \exp\left(-D\alpha_n^2 t\right). \tag{5.23}$$

The corresponding solution useful for small times is

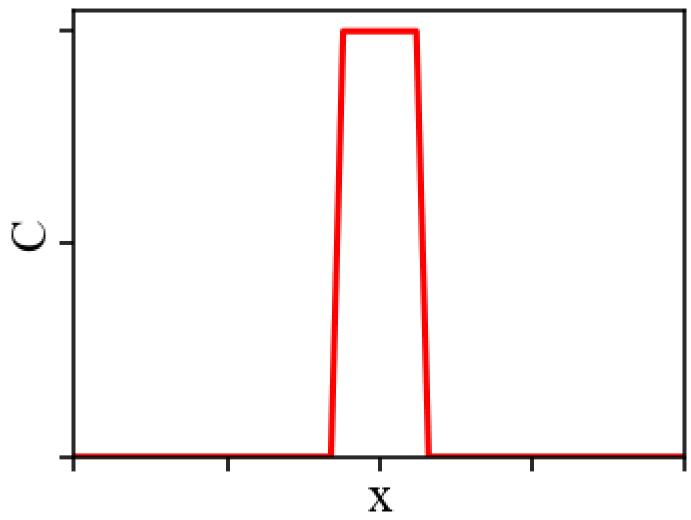
$$\frac{C-C_1}{C_0-C_1} = \frac{a^{\frac{1}{2}}}{r^{\frac{1}{2}}} \operatorname{erfc} \frac{a-r}{2\sqrt{(Dt)}} + \frac{(a-r)(Dta)^{\frac{1}{2}}}{4ar^{\frac{3}{2}}} \operatorname{ierfc} \frac{a-r}{2\sqrt{(Dt)}} + \frac{(9a^2-7r^2-2ar)Dt}{32a^{\frac{3}{2}}r^{\frac{5}{2}}} \operatorname{i^2erfc} \frac{a-r}{2\sqrt{(Dt)}} + \dots, \tag{5.24}$$

which holds provided $r/a$ is not small. The case of $r/a$ small is discussed by Carsten and McKerrow (1944). They give a series solution involving modified Bessel functions of order $n \pm \frac{1}{4}$. The necessary functions are tabulated in their paper and numerical calculation is straightforward.

Crank, J. (1975) The Mathematic of Diffusion. 2nd ed., Claredon Press, Oxford, U.K., 255.

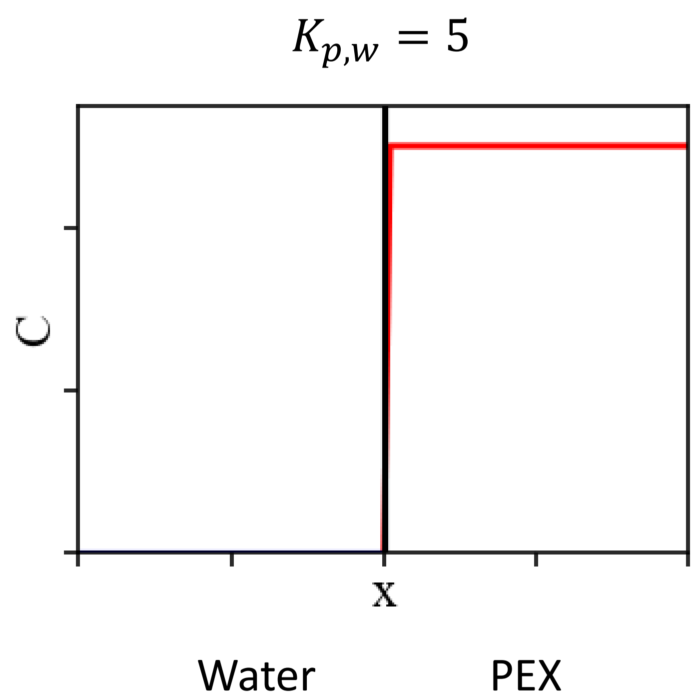
# *Diffusion Coefficient, D*

- Mass flows downhill.
- Diffusion is a smoothing function.
- $D$ decreases with contaminant size.
- $D$ decreases with polymer crystallinity.



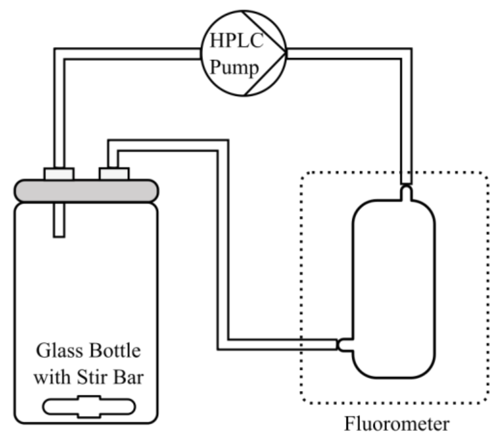
# Partition Coefficient, $K_{p,w}$

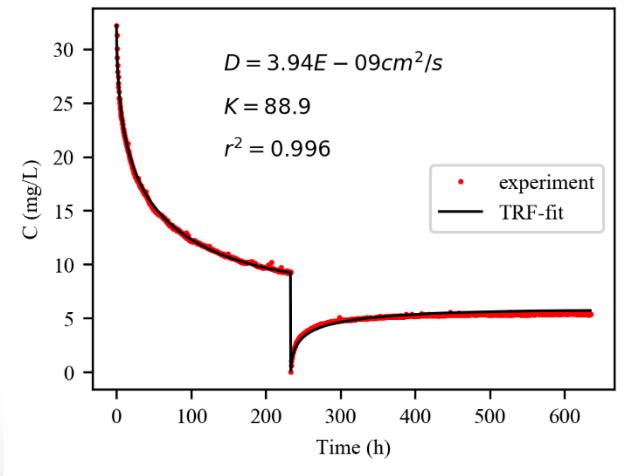
- Some contaminants prefer one medium over another.
- $K_{p,w}$ for large pesticides can be as high as $10^5$.



# Experimental Approach: Determining $D$ and $K_{p,w}$

- Analyte: Toluene
  - Easily detected by fluorescence
  - Soluble (enough) in water and polyethylene
  - Representative of several BTEX contaminants
- Polymer: Cross-Linked Polyethylene (PEX)

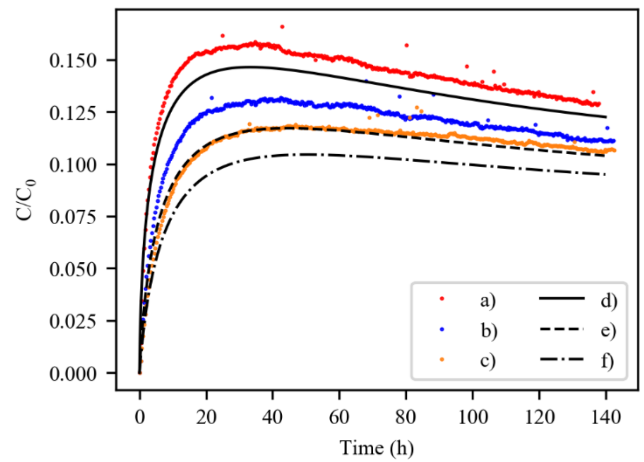


# Experimental Approach: Flushing Simulation

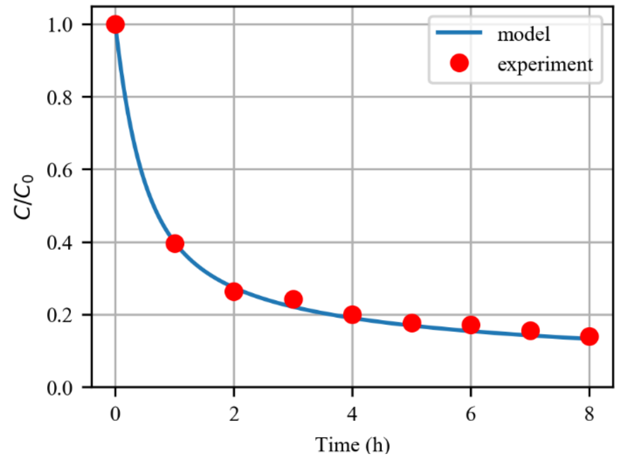
- Rinsed contaminated pipe segments with tap water.
- Rinsing Times:
  - a) 2 minutes
  - b) 1 hour
  - c) 2 hours
- 8% under-prediction. Likely because rinsing in a sink isn't the same as flushing with infinite water.
- ~3% error otherwise.

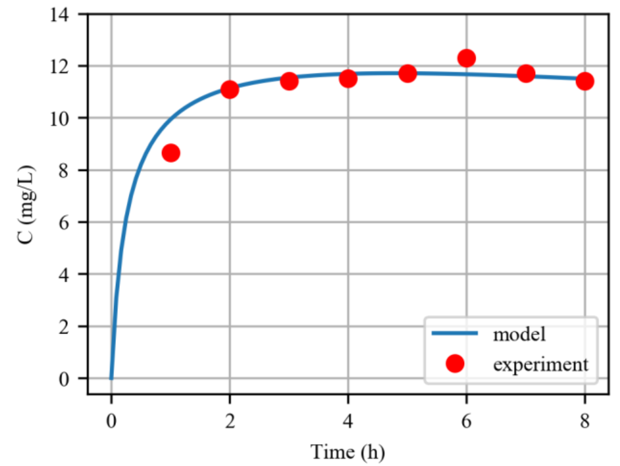
Post-rinse Extraction



# Experimental Approach: Stagnant (De)sorption

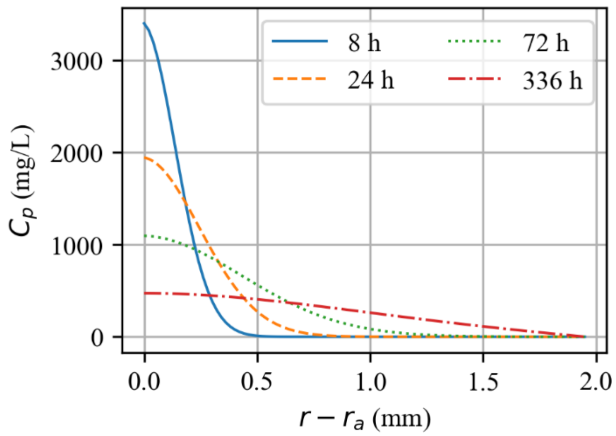
- Pipe segments are sealed with contaminated water inside.
- The samples are sacrificed to observe concentration over time.
- Mean Absolute error ~3.1%
- Explicit treatment of diffusion in water seems unnecessary in this case.



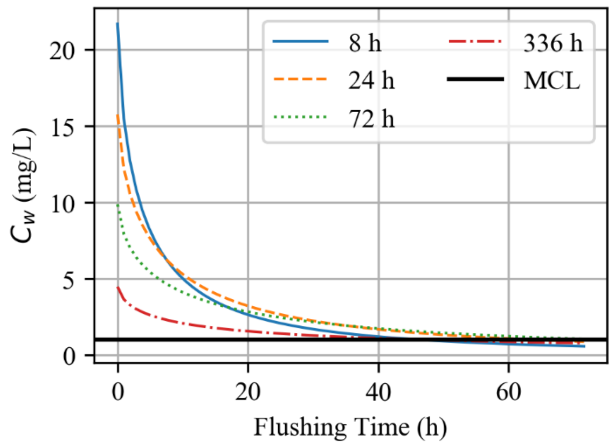



# Toluene Contamination Scenario

- Stagnant contamination of 3/8" PEX-a by 300 mg/L toluene.
- Flushing time required to decontaminate pipe is predicted to be more than 40 hours.
- Two days of flushing is a lot of water!




Stagnant Pipe wall profiles

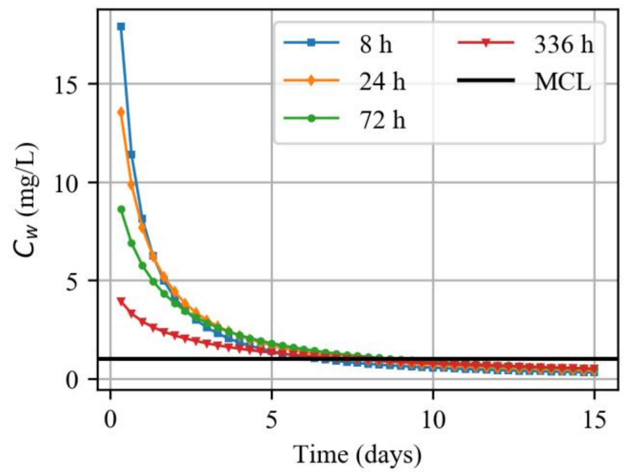



Overnight Water Recontamination After Flushing

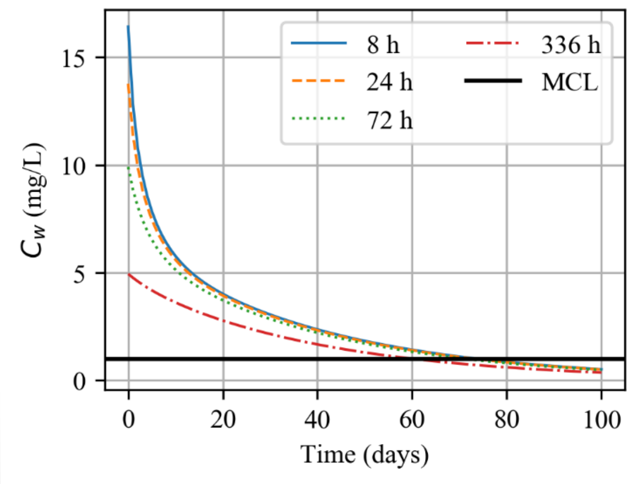
- (1 mg/L)

# Alternate Strategies

- Flushing for 30 minutes every 8 hours reduces the water used, but extends treatment time by several days.
- Relying on toluene volatility alone would save water, but would also require months of waiting.



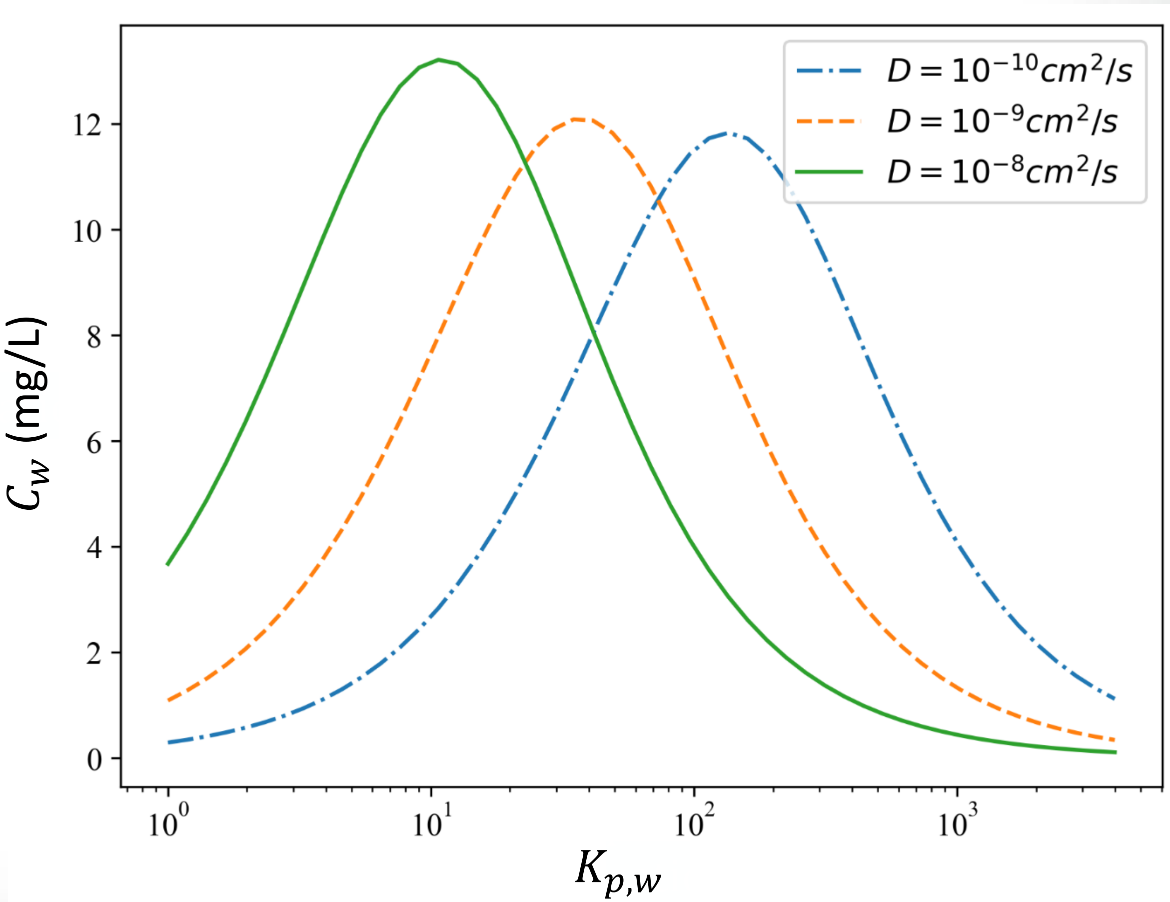

Flush 30 min. every 8 h




Volatility only

# Other Contaminants: Is 30 Minutes of Flushing Enough?

- Model can be extended to other organic contaminants if $D$ and $K_{p,w}$ are known.
- $C_{initial}$= 100 mg/L
- 8-hour stagnation time
- 30-minute flushing time
- $C_w$ = expected contaminant concentration in clean water after being left overnight.



# Other Plastics?

- Predictions should be valid for polyethylene pipes, including HDPE, PEX, LDPE, etc.
- Polypropylene should behave similarly.
- PVC, unfortunately, exhibits anomalous diffusion.

# Conclusions

- Polyethylene pipes can act as reservoirs for some organic contaminants.
- Depending on contaminant properties and severity of exposure, 30 minutes of flushing may not be sufficient for remediation.
- For extensive contamination, even weeks of constant flushing may be inadequate.
- These considerations will become increasingly important as polyethylene continues to replace less permeable plumbing materials.

# Future Work

- Investigate variance in parameters across pipes. Preliminary results suggest $D$ can vary by 20% or more between PE from different manufacturers.
- Find methods to estimate $D$ and $K_{p,w}$ for unstudied pipe/contaminant combinations; experiments are time-consuming.

# Thank You

**Diffusion within polymer pipes may significantly impact decontamination.**

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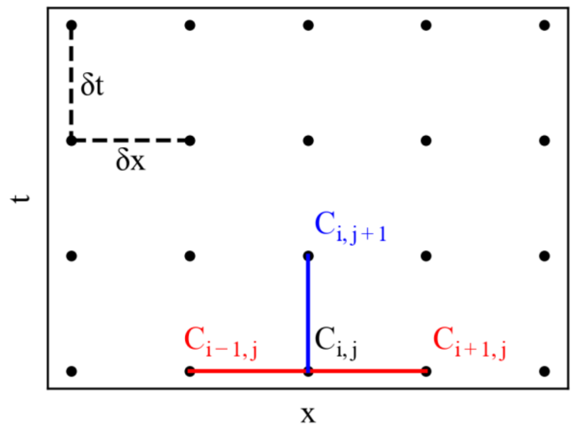
***Disclaimer:*** *The U.S. Environmental Protection Agency through its Office of Research and Development funded the research described here. It has been subjected to the Agency's review and has been approved for public presentation. EPA does not endorse the purchase or sale of any commercial products or services. This project was supported in part by an appointment to the Research Participation Program at US EPA, administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and EPA.*

# Bonus Slides

# Finite Difference Method

$$\left(\frac{\partial C}{\partial t}\right)_{\mathrm{i,j}} \approx \frac{C_{i,j+1} - C_{i,j}}{\delta t}$$

$$\left(\frac{\partial^2 C}{\partial x^2}\right)_{\mathrm{i,j}} \approx \frac{C_{i+1,j} - 2C_{i,j} + C_{i-1,j}}{(\delta x)^2}$$




Remembering that

$$\left(\frac{\partial C}{\partial t}\right)_{\mathrm{i,j}} = D\left(\frac{\partial^2 C}{\partial x^2}\right)_{\mathrm{i,j}}$$

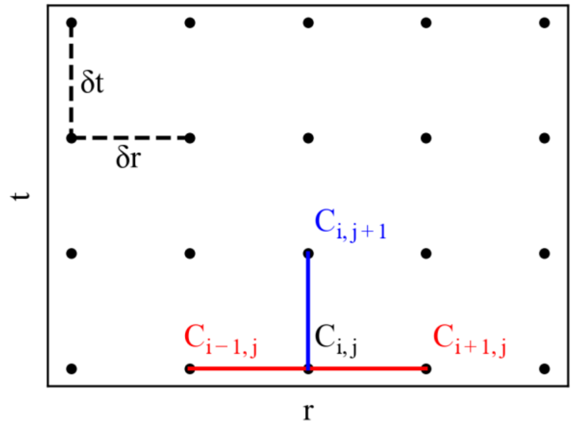
we can now solve the inner grid points.

$$C_{i,j+1} = C_{i,j} + \frac{D\delta t}{(\delta x)^2}\left(C_{i+1,j} - 2C_{i,j} + C_{i-1,j}\right)$$

# Radial Geometry

For situations where a pipe wall isn't well modeled by an infinite plane sheet, we need to convert to cylindrical coordinates.

$$\left(\frac{\partial^2 C}{\partial x^2}\right)_{\mathrm{i,j}} \rightarrow \left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right)_{i,j}$$

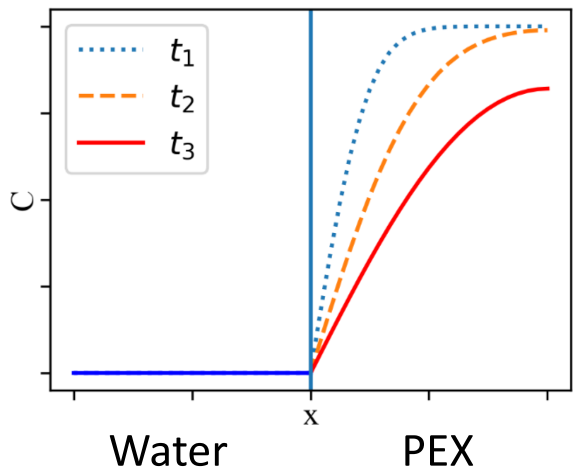



$$\left(\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r}\right)_{i,j} \approx \frac{1}{2i(\delta r)^2}\{(2i+1)C_{i+1,j} - (4i)2C_{i,j} + (2i-1)C_{i-1,j}\} \quad i \neq 0$$

Basically, we correct by scaling with the circumference. We handle the hollow cylinder by offsetting $i$ appropriately.

# Boundary Conditions (I)

- Flushing case is handled simply.
- An infinite stream of clean water is modeled by setting $C_{0,j}$ to zero.
- Real flushing will be slightly slower.



# Boundary Conditions (II)

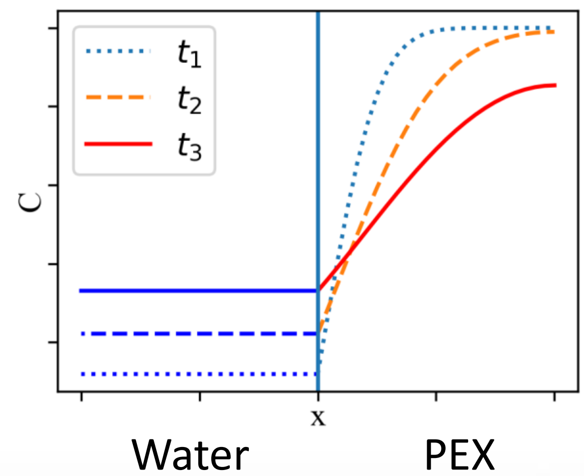
- The case of extraction/leaching is more complicated.
- $J$ = mass flux
- $A$ = contact area
- $V_w$= volume of well-stirred solution
- $C_w$= concentration in well-stirred solution
- $C_p$= concentration in the polymer

Remembering that

$$J = -D\frac{\partial C}{\partial x}$$

We balance mass by setting

$$V_w\frac{\partial C_w}{\partial t} = -AD\frac{\partial C_p}{\partial x}, x = 0$$



# Heavily Contaminated Pipe

- Repeated, long term exposure can cause uniform contaminant distribution in pipe wall.
- Decontamination by flushing may take weeks or months.
- Decontamination is much faster if contaminant can escape through outer wall.
- Treatment time scales with square of pipe wall thickness.