Predicting Effectiveness of Removal of Organic Contaminants from Polyethylene Pipes by Flushing

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International Decontamination Research and Development Conference
Research Triangle Park, NC

May 10, 2018
Flush 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?

Plastic Pipes

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

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 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

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

The corresponding solution useful for small times is

$$\frac{C - C_1}{C_0 - C_1} = \frac{a^3}{r^3} \text{erfc} \frac{a-r}{2\sqrt{Dt}} + \frac{(a-r)(Dta)}{4ar^3} \text{ierfc} \frac{a-r}{2\sqrt{Dt}}$$

$$+ \frac{(9a^2 - 7r^2 - 2ar)Dtr}{32a^3r^3} i^2 \text{erfc} \frac{a-r}{2\sqrt{Dt}} + \ldots, \quad (5.24)$$

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.

**Diffusion Coefficient, $D$**

- Mass flows downhill.
- Diffusion is a smoothing function.
- $D$ decreases with contaminant size.
- $D$ decreases with polymer crystallinity.
Some contaminants prefer one medium over another. $K_{p,w}$ for large pesticides can be as high as $10^5$. 

Partition Coefficient, $K_{p,w}$
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)**

![Diagram of experimental setup](image)
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.
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 $\sim 3.1\%$
- Explicit treatment of diffusion in water seems unnecessary in this case.
Toluene Contamination Scenario

- Stagnant contamination of 3/8” PEX-a by 400 mg/L toluene.
- Flushing time required to decontaminate pipe is predicted to be more than 40 hours.
- The problem may resolve itself after a month or two of regular use.
- However, we are only considering contamination from a single pipe volume . . .
Heavily Contaminated Pipe

- If $C_p$ is uniform, which can happen following repeated, long term exposure, decontamination by flushing may take weeks or months.
- If the contaminant can escape through the outer skin of the pipe, decontamination time is reduced considerably.
- Treatment time scales with square of pipe wall thickness.
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
• $C_w = \text{expected contaminant concentration in clean water after being left overnight.}$
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.
Diffusion within polymer pipes may significantly impact decontamination.

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Finite Difference Method

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

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

Remembering that

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

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.

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

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

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.
- \( J = \text{mass flux} \)
- \( A = \text{contact area} \)
- \( V_w = \text{volume of well-stirred solution} \)
- \( C_w = \text{concentration in well-stirred solution} \)
- \( C_p = \text{concentration in the polymer} \)

Remembering that

\[
J = -D \frac{\partial C}{\partial x}
\]

We balance mass by setting

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