

# **AOS 104**

## **Fundamentals of Air and Water Pollution**

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### **Grades**

<b>Homework</b>	<b>150 pts</b>
<b>2 Midterms</b>	<b>300 pts</b>
<b>Final Exam</b>	<b>550 pts</b>
<b>Total</b>	<b>1000 pts</b>

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### **Homework**

- **There will be 6 homework sets**
- **Homework is due by the end of business (~ 5 pm) on the due date**
- **Late homework will receive partial credit as outlined in the syllabus**
- **You are encouraged to work together and discuss approaches to solving problems, but must turn in your own work**

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# Lecture Notes

**ADS 104**  
**Fundamentals of Air and Water Pollution**

Grades	
Midterm	40%
Exam 1	20%
Exam 2	20%
Final Exam	20%
Total	100%

**Homework**

- There will be homework sets.
- Assignment to due at the beginning of class.
- Late assignments will be marked as zero.
- The homework sets will be graded and returned to you.

**Overview of Topics**

- Measurement of concentration
- Effects of pollution on water quality and on air
- Types of air pollution
- Urban air pollution
- Stratospheric air pollution
- Global climate change

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## Topics of the course

- **Calculating pollution concentration**
- **Effects of pollution on acidity (pH)—acid rain**
- **Types of water pollution**
  - **Health effects from water pollution**
- **Types of air pollution**
  - **Health effects of air pollution**
- **Urban air pollution—bad ozone**
- **Stratospheric air pollution—depletion of good ozone**
- **Global climate change**

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## Introduction

- **Measurement of Concentration**
  - **Liquids**
  - **Air**
  - **Conversions Involving the Ideal Gas Law**
- **Material Balance Models**
  - **Basics**
  - **Steady-state Model With Conservative Pollutants**
  - **Residence Time**
  - **Steady and Non-steady Models With Non-conservative Pollutants**

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# Units of Measurement

- **Both SI and British units used**

→ **Be able to convert between these two standards**

→ **Examples**

Quantity	SI	British
Length	m	ft
Volume	m <sup>3</sup>	ft <sup>3</sup>
Power	watt	BTU/hr
Density	kg/m <sup>3</sup>	lb/ft <sup>3</sup>

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# Concentration

- **The amount of a specified substance in a unit amount of another substance**

→ **Usually, the amount of a substance dissolved in water or mixed with the atmosphere**

- **Can be expressed as...**

Mass/Mass	g/kg, lb/ton, ppm, ppb
Mass/Volume	g/L, $\mu\text{g}/\text{m}^3$
Volume/Volume	mL/L, ppmv, ppbv
Volume/Mass	L/kg
Moles/Volume	molarity, M, mol/L

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# Liquids

**Concentrations of substances dissolved in water are generally given as mass per unit volume.**

**e.g., milligrams/liter (mg/L) or micrograms/liter ( $\mu\text{g}/\text{L}$ )**

**Concentrations may also be expressed as a mass ratio, for example:**

**7 mass units of substance A per million mass units of substance B is 7 ppm.**

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### Example 1

23  $\mu\text{g}$  of sodium bicarbonate are added to 3 liters of water.

What is the concentration in  $\mu\text{g/L}$  and in ppb (parts per billion) and in moles/L?

$$\frac{23 \mu\text{g}}{3 \text{ L}} = 7.7 \frac{\mu\text{g}}{\text{L}}$$

To find the concentration in ppb we need the weight of the water.

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Standard assumption: density of water is 1g/ml or 1000 g/L (at 4°C).

$$\frac{7.7 \times 10^{-6} \text{ g}}{1 \text{ L}} \times \frac{1 \text{ L}}{1000 \text{ g}} = 7.7 \times 10^{-9} = \frac{7.7}{10^9} = \frac{7.7}{\text{billion}} = 7.7 \text{ ppbm}$$

⇒ For density of water is 1000 g/L,

$$1 \mu\text{g/L} = 1 \text{ ppbm}$$

$$1 \text{ mg/L} = 1 \text{ ppm}$$

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Sometimes, liquid concentrations are expressed as mole/L (M).

e.g., concentration of sodium bicarbonate ( $\text{NaHCO}_3$ ) is 7.7  $\mu\text{g/L}$

$$\begin{aligned} \text{Molecular Weight} &= [23 + 1 + 12 + (3 \times 16)] \frac{\text{g}}{\text{mol}} \\ &= 84 \frac{\text{g}}{\text{mol}} \end{aligned}$$

$$\begin{aligned} \text{Molar Concentration} &= \frac{7.7 \mu\text{g}}{1 \text{ L}} \times \frac{1 \text{ mol}}{84 \text{ g}} \times \frac{1 \text{ g}}{1 \times 10^6 \mu\text{g}} \\ &= 9.2 \times 10^{-8} \frac{\text{mol}}{\text{L}} \end{aligned}$$

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# Air

**Gaseous pollutants—use volume ratios:  
ppmv, ppbv**

**Or, mass/volume concentrations—use  $m^3$   
for volume**

## Example 2

**A car is running in a closed garage. Over 3 minutes, it expels 85 L of CO. The garage is 6 m  $\times$  5 m  $\times$  4 m. What is the resulting concentration of CO? Assume that the temperature in the room is 25°C.**

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## Solution:

**The volume of CO is 85 L and**

$$\begin{aligned}\text{Volume of room} &= 6 \text{ m} \times 5 \text{ m} \times 4 \text{ m} \\ &= 120 \text{ m}^3 \\ &= 120000 \text{ L}\end{aligned}$$

$$\begin{aligned}\text{Concentration} &= \frac{85 \text{ L}}{120000 \text{ L}} = 0.000708 = 708 \times 10^{-6} \\ &= 708 \text{ ppmv}\end{aligned}$$

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## Example 2 Cont.

**Instead of 85 L of CO, let's say 3 moles of CO were emitted.**

**We need to find the volume occupied by three moles of CO.**

IDEAL GAS LAW:  $PV = nRT$

P = Pressure (atm)

V = Volume (L)

n = Number of moles

R = Ideal Gas Constant =  $0.08206 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

T = Temperature (K)

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**To remember the units it's  
All Lovers Must Kiss**  
(atm, L, mol, K)

**This law tells you how a gas responds to a  
change in its physical conditions. Change P,  
V or T, and the others adjust**

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## **The Ideal Gas Law**

$$PV = nRT$$

so  $P_1V_1 = nRT_1$   $P_2V_2 = nRT_2$  etc.

**Can rearrange to get the equality,**

$$\frac{P_1V_1}{T_1} = nR = \frac{P_2V_2}{T_2}$$

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**The ideal gas law also tells you that:**

- ▶ **at 0°C (273 K) and 1 atm (STP),  
1 mole occupies 22.4 L**
- ▶ **at 25°C (298 K) (about room temperature)  
and 1 atm,  
1 mole occupies 24.5 L**

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## Back to Example 2

$$\text{Volume of CO} = (3 \text{ mol}) \left( 24.5 \frac{\text{L}}{\text{mol}} \right) = 73.5 \text{ L}$$

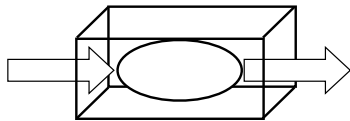
$$\begin{aligned} \text{Volume of room} &= 6 \text{ m} \times 5 \text{ m} \times 4 \text{ m} \\ &= 120 \text{ m}^3 = 120000 \text{ L} \end{aligned}$$

$$\begin{aligned} \text{Concentration} &= \frac{73.5 \text{ L}}{120000 \text{ L}} \\ &= 0.000613 \\ &= 613 \times 10^{-6} = 613 \text{ ppmv} \end{aligned}$$

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## Material Balances

- Expresses *Law of Conservation of Mass*
- Material balances can be applied to many systems—organic, inorganic, steady-state, financial, etc.



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### Basic equation of material balance

$$\text{Input} = \text{Output} - \text{Decay} + \text{Accumulation}$$

(eq. 1.11)

Input, output, etc. are usually given as rates, but may also be quantities (i.e. masses).

- ⇒ This equation may be written for the overall system, or a series of equations may be written for each component and the equations solved simultaneously.

Steady-state (or equilibrium), conservative systems are the simplest

- ⇒ Accumulation rate = 0, decay rate = 0

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## Example 3

**Problem 1.7 – Agricultural discharge containing 2000 mg/L of salt is released into a river that already has 400 ppm of salt. A town downstream needs water with <500 ppm of salt to drink. How much clean water do they need to add?**

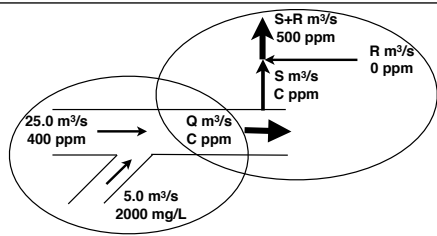
**Maximum recommended level of salts for drinking water = 500 ppm.**

**Brackish waters have > 1500 ppm salts.**

**Saline waters have > 5000 ppm salts.**

**Sea water has 30,000–34,000 ppm salts.**

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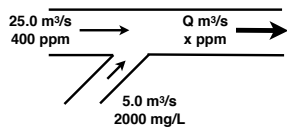
**What is the concentration in flow Q?**

**What flow of clean water (R) must be mixed to achieve 500 ppm?**

**(What is the ratio of R/S?)**

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**To simplify, we can break this into two systems—first (remembering that 1 ppm = 1 mg/L)**



**Basic equation: input = output**

$$(25.0 \frac{\text{m}^3}{\text{s}} \times 400 \text{ ppm}) + (5.0 \frac{\text{m}^3}{\text{s}} \times 2000 \text{ ppm}) = (Q \frac{\text{m}^3}{\text{s}} \times C \text{ ppm})$$

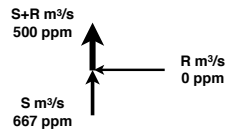
$$Q = \text{Total flow} = 25.0 \frac{\text{m}^3}{\text{s}} + 5.0 \frac{\text{m}^3}{\text{s}} = 30.0 \frac{\text{m}^3}{\text{s}}$$

**Thus, C = the salt concentration at the take-out from the river = 667 ppm**

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**Solve the other part of the system:**



$$\left[ S \frac{\text{m}^3}{\text{s}} \times 667 \text{ ppm} \right] + \left[ R \frac{\text{m}^3}{\text{s}} \times 0 \text{ ppm} \right] = (S + R) \frac{\text{m}^3}{\text{s}} \times 500 \text{ ppm}$$

$$667S = 500S + 500R$$

$$\frac{R}{S} = \frac{667 - 500}{500} = 0.33$$

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## Residence Time

• **Lifetime or residence time of substance**  
 ≡ amount / rate of consumption

• **Lifetime of Earth's petroleum resources:**

$$1.0 \times 10^{22} \text{ J} / 1.35 \times 10^{20} \text{ J/yr} = 74 \text{ years}$$

ANWR has ~5.7 to  $16.3 \times 10^9$  barrels of oil; best guess is  $10 \times 10^9$ . The US consumes 19 million barrels/day of oil. How much time does this give us?



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• **The residence time may be defined for a system in *steady-state* as:**

$$\frac{\text{Stock (material in system)}}{\text{Flow rate (in or out)}}$$

• **Residence time in a lake: The average time water spends in the lake**

• **Some water may spend years in the lake**

• **Some may flow through in a few days**

⇒ **Depends on mixing.**

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- In the first approximation, consider only stream flow in and stream flow out.

$$T = M/F_{in} = M/F_{out}$$

For this very simple steady state system, we calculate the residence time

Ex. The volume of a lake fed by a stream flowing at  $7 \times 10^5 \text{ m}^3/\text{day}$  is  $3 \times 10^8 \text{ m}^3$ . What is the residence time of the water in the lake?

$$\frac{3 \times 10^8 \text{ m}^3}{7 \times 10^5 \frac{\text{m}^3}{\text{day}}} = 430 \text{ days}$$

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## More Material Balances

- What if a substance is removed by chemical, biological or nuclear processes?

→ The material is still in steady-state if its concentration is not changing.

- Steady-state for a non-conservative pollutant:

→ We now need to include the decay rate in our material balance expression:

$$\text{Input rate} = \text{Output rate} + \text{Decay rate}$$

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Assume decay is proportional to concentration ("1<sup>st</sup> order decay").

$$\frac{dC}{dt} = -kC$$

where  $k$  = reaction rate coefficient, in units of 1/time.

$C$  = concentration of pollutant

Separate variables and integrate:

$$\int_{C_0}^C \frac{dC}{C} = \int_0^t -k dt$$

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**Solution:**  $\ln(C) - \ln(C_0) = -kt - \cancel{kt_0}$

$$\ln(C) - \ln(C_0) = \ln\left(\frac{C}{C_0}\right) = -kt$$

Take the exponential of each side:

$$C = C_0 e^{-kt}$$

For a particular system (i.e., a lake), we can write a total mass decay rate (mass/time), that we can compare with the input and output rates:

$$= kCV \Rightarrow \text{mass removal rate}$$

**k** has units of 1/time  
**C** has units of mass/volume  
**V** has units of volume

Thus the decay rate = **kCV** (mass/time)

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## Material Balance Equation

Steady state with decay

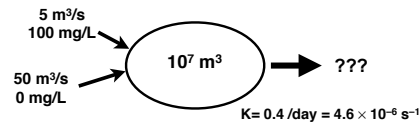
$$\text{Input rate} = \text{Output rate} + kCV$$

Example 4

A lake with a constant volume of  $10^7 \text{ m}^3$  is fed by a clean stream at a flow of  $50 \text{ m}^3/\text{s}$ . A factory dumps  $5.0 \text{ m}^3/\text{s}$  of a non-conservative pollutant with a concentration of  $100 \text{ mg/L}$  into the lake. The pollutant has a reaction (decay) rate coefficient of  $0.4/\text{day}$  ( $= 4.6 \times 10^{-6} \text{ s}^{-1}$ ). Find the steady-state concentration of the pollutant in the lake.

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Start by drawing a diagram of the problem statement.



**Solution:**  
 Assume the volume of the lake is constant, so the outflow is equal to the inflow, or

$$\text{Water outflow rate} = 55 \text{ m}^3/\text{s}$$

For the pollutant:

$$\text{Input rate} = \text{Output rate} + \text{Decay rate}$$

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### Variation—Non-steady situation

Consider a lake that initially had zero concentration of the pollutant, and then a pollutant was introduced. How is the concentration changing with time? (i.e., a transient phenomenon—not steady-state)

#### Step function response

Mass balance:

$$\text{Accumulation rate} = \text{Input rate} \\ - \text{Output rate} \\ - \text{Decay rate}$$

$$V \frac{dC}{dt} = S - QC - kCV$$

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Eventually system reaches a steady-state concentration,  $C(\infty)$  (i.e., when  $dC/dt = 0$ )

$$C(\infty) = C_{\infty} = \frac{S}{Q + kV}$$

Concentration as a function of time (before steady-state is reached) is given by the transient equation:

$$\frac{dC}{dt} = \frac{S}{V} - \frac{QC}{V} - kC$$

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which can be rearranged to give:

$$\frac{dC}{dt} = -\left(k + \frac{Q}{V}\right)\left[C - \frac{S}{Q + kV}\right]$$

So we can substitute for  $C_{\infty}$ :

$$\frac{dC}{dt} = -\left(k + \frac{Q}{V}\right)[C - C_{\infty}]$$

To integrate, we simplify the  $C - C_{\infty}$  term:

$$y = C - C_{\infty} \Rightarrow \frac{dy}{dt} = \frac{dC}{dt}$$

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$$\frac{dy}{dt} = -\left(k + \frac{Q}{V}\right)y$$

⇒ a familiar, separable differential equation ( $k+Q/V$  is a constant!), with a solution of the form:

$$y = y_0 e^{-\left(k + \frac{Q}{V}\right)t} \text{ where } y_0 = C_0 - C_\infty$$

Substituting and rearranging,

$$C(t) = C_\infty + (C_0 - C_\infty) \exp\left[-\left(k + \frac{Q}{V}\right)t\right]$$

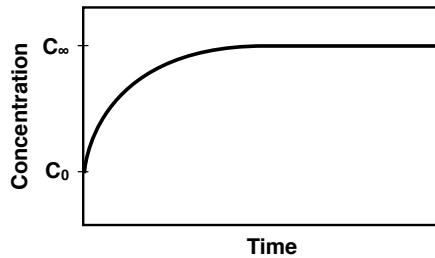
At  $t = 0$ ,  $\exp = 1$   
 $t = \infty$ ,  $\exp = 0$

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$$C(t) = C_\infty + (C_0 - C_\infty) \exp\left[-\left(k + \frac{Q}{V}\right)t\right]$$

What is the general behavior of this equation?  
 At time = 0, the exponential term goes to 1 so  
 $C = C(0)$

At time =  $\infty$ ,  $\exp$  goes to 0 ⇒  $C = C_\infty$



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### Example 5

Bar with volume of 500 m<sup>3</sup>

Fresh air enters at a rate of 1000 m<sup>3</sup>/hr  
 Bar is clean when it opens at 5 PM

Formaldehyde is emitted at 140 mg/hr after 5 PM by smokers

$k$  = the formaldehyde removal rate coeff. = 0.40/hr

What is the concentration at 6 PM?

$$C(t) = (C(0) - C_\infty) \exp\left[-\left(k + \frac{Q}{V}\right)t\right] + C_\infty$$

Solution—First we need  $C_\infty$

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**Q = 1000 m<sup>3</sup>/hr; V = 500 m<sup>3</sup>; S=140 mg/hr;  
k = 0.40 /hr**

$$C_{\infty} = \frac{S}{Q + kV} = \frac{140.0 \text{ mg/hr}}{1000.0 \text{ m}^3/\text{hr} + (0.4/\text{hr} \times 500 \text{ m}^3)}$$

$$C_{\infty} = 0.117 \text{ mg/m}^3$$

**For the concentration at 6 PM, one hour after the bar opens, substitute known values into:**

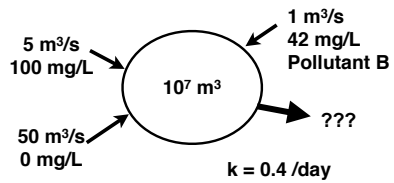
$$C(t) = (C_0 - C_{\infty})\exp\left[-\left(k + \frac{Q}{V}\right)t\right] + C_{\infty}$$

$$C(t) = \left(0 - 0.117 \frac{\text{mg}}{\text{m}^3}\right)\exp\left[-\left(0.40 \frac{1}{\text{hr}} + \frac{1000.0 \frac{\text{m}^3}{\text{hr}}}{500.0 \text{m}^3}\right)t\right] + 0.117 \frac{\text{mg}}{\text{m}^3}$$

$$C(t) = 0.117 \frac{\text{mg}}{\text{m}^3}(1 - e^{-2.4t})$$

$$C(1 \text{ hr}) = 0.117 \frac{\text{mg}}{\text{m}^3}(1 - e^{-2.4}) = 0.106 \text{ mg/m}^3$$

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**New factory opens, discharging pollutant B.  
If k is 0.4/day, what is the concentration  
after 2 days of discharges?**

$$S = \left(1 \frac{\text{m}^3}{\text{s}}\right)\left(1000 \frac{\text{L}}{\text{m}^3}\right)\left(86400 \frac{\text{s}}{\text{day}}\right)\left(42 \frac{\text{mg}}{\text{L}}\right) = 3.628 \times 10^9 \frac{\text{mg}}{\text{day}}$$

$$Q = \left((50 + 5 + 1) \frac{\text{m}^3}{\text{s}}\right)\left(1000 \frac{\text{L}}{\text{m}^3}\right)\left(86400 \frac{\text{s}}{\text{day}}\right) = 4.838 \times 10^9 \frac{\text{L}}{\text{day}}$$

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**V = 10<sup>7</sup> m<sup>3</sup>  
Q = 4.838 × 10<sup>9</sup> L/day  
S = 3.628 × 10<sup>9</sup> mg/day  
k = 0.4/day  
C = \_\_\_\_\_**

$$C(t) = C_{\infty} + (C_0 - C_{\infty})\exp\left[-\left(k + \frac{Q}{V}\right)t\right]$$

$$C_{\infty} = \frac{S}{Q + kV}$$

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**First step:**

$$\begin{aligned}C_{\infty} &= \frac{S}{Q + KV} \\&= \frac{3.628 \times 10^9 \frac{\text{mg}}{\text{day}}}{4.838 \times 10^9 \frac{\text{L}}{\text{day}} + 0.4 \frac{1}{\text{day}} \times 10^{10} \text{ L}} \\&= 0.410 \text{ mg/L}\end{aligned}$$

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**Now use step function to find concentration at 2 days**

$$C(t) = C_{\infty} + (C_0 - C_{\infty}) \exp\left[-\left(k + \frac{Q}{V}\right)t\right]$$

$$C_0 = 0;$$

$$C(t) = \left[1 - \exp\left[-\left(k + \frac{Q}{V}\right)t\right]\right] C_{\infty}$$

$$= \left[1 - \exp\left[-\left(0.4 \frac{1}{\text{day}} + \frac{4.84 \times 10^9 \frac{\text{m}^2}{\text{day}}}{10^{10} \text{ m}^3}\right) 2 \text{ days}\right]\right] \left(0.41 \frac{\text{mg}}{\text{L}}\right)$$

$$= (0.829) 0.41 \frac{\text{mg}}{\text{L}}$$

$$= 0.34 \text{ mg/L}$$

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