# Environmental Fate & Transport

## 40 CFR Part 158, Subpart W

US EPA

# Background

- Before 158W, OPP characterized many antimicrobial uses as “indoor uses” ; Many of these “indoor uses” had potential to be released down-the-drain and subsequently enter environmental media, but exposures and risk were not being considered
- Purpose of presentation: Provide a broad overview of environmental fate and transport processes, including:
  - Chemical Degradation
  - Microbial Degradation
  - Intermedia Transport
  - Wastewater Treatment Plant (WWTP) fate
- Provide information on the role of physical/chemical properties and WWTP effects data in determining environmental fate data requirements

# Background (cont'd)

- Environmental fate data provide information on:
  - Persistence in soil/sediment and water under aerobic and anaerobic conditions
  - Sorption (attachment) to soil and sediment
  - Leaching (removal) from treated wood and boat paints
  - Exposure from ballast water
- Wastewater Treatment Plant (WWTP) data on fate and effects include information on:
  - Biodegradation during wastewater treatment
  - Sorption to activated sludge
  - Toxicity to activated sludge microorganisms

# Elements of Environmental Fate Assessment

- Chemical degradation in environmental media like air, water, soil, sediment.
- Microbial degradation in these media
- Transport in environmental media
- Fate in and release from WWTPs
- Ballast water, antifoulant paints, and wood preservative scenarios require more fate data than other uses

# 12 Major Use Patterns

1. Agricultural Premises & Equipment
2. Food Handling/Storage Establishments, Premises and Equipment
3. Commercial, Institutional and Industrial Premises and Equipment
4. Residential and Public Access Premises
5. Medical Premises and Equipment
6. Human Drinking Water Systems
7. Materials Preservatives
8. Industrial Processes and Water Systems
9. Antifoulant Coatings and Ballast Water Treatments
10. Wood Preservatives
11. Swimming Pools and Spas
12. Aquatic Areas

# 12 Use Sites Grouped into 5 Major Sites (Based on Fate Table in 158W)

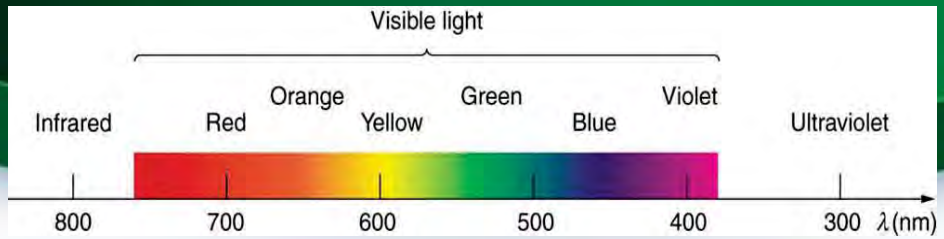
- Industrial processes and water systems
- Antifoulant coatings and paints
- Wood preservatives
- Aquatic areas
- All other use patterns

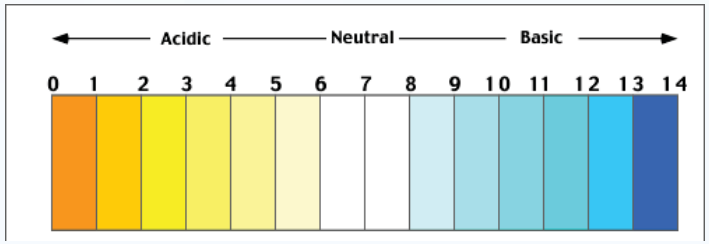
# Degradation Processes and Types of Tests

- Types of degradation processes: Chemical (abiotic) and microbial (biotic)
- Chemical degradation: 30 day tests
  - Hydrolysis (835.2120)
  - Photodegradation in water (835.2240)
  - Photodegradation on soil (835.2410)

# Chemical Degradation

- Hydrolysis (835.2120)
  - Is conducted in darkness
  - Required for all pesticides
  - Measures degradation in water at pH 5, 7, and 9 (OECD uses pH 4)
  - Range of pH represents environmental pH values
  - Identifies degradation products and their formation and decline rates




# Chemical Degradation

- Photodegradation in Water (835.2240)
  - Measures degradation in water by sunlight at pH at which the compound is hydrolytically stable
  - Identifies degradation products and their formation and decline rates
  - May be waived if compound does not absorb ultraviolet (UV) light between 290 and 800 nm in wavelength
  - 290-800 nm range represents sunlight range
  - May be waived if compound is not stable at pH 5, 7, and 9 in hydrolysis study

# Chemical Degradation

- Photodegradation in Soil (835.2410)
  - Measures transformation on soil surfaces by light
  - Identifies phototransformation products formed and their formation and decline rates
  - May be waived if compound does not absorb ultraviolet (UV) light between 290 and 800 nm in wavelength

# Chemical Reactions that Degrade Pesticides

| | | Does the study contain? | | |
|---|---|---|---|---|
| **Test Guideline** | **Guideline Number** | **Water** | **Light** | **Soil** |
| Hydrolysis | 161-1<br>835.2120 | Yes | No | No |
| Photodegradation in Water | 161-2<br>835.2240 | Yes | Yes | No |
| Photodegradation on soil | 161-3<br>835.2410 | Yes | Yes | Yes |

Results of fate studies are ADDITIVE to make a bigger picture

# Microbial Degradation (or Biotic Conditions)

- Aerobic soil metabolism (835.4100) ≤ 1 yr
- Anaerobic soil metabolism (835.4200) ≤ 1 yr
- Aerobic aquatic metabolism (835.4300) 30-60 days
- Anaerobic aquatic metabolism (835.4400) ≤ 1 yr

# Aerobic Soil Metabolism

- Represents top layer of soil after drying following rain (top 3-4 cm)
- Transformation of a pesticide in soil in the presence of oxygen (hence aerobic)
- Measures transformation of parent compound and formation and decline rates of transformation products

# Anaerobic Soil Metabolism

- Represents metabolism of pesticide in soil in absence of oxygen
- Transformation of a pesticide in lower layers of soil or the saturated top layer of soil immediately after a rain event in the absence of oxygen.
- Measures transformation of parent compound and formation and decline rates of degradation products

# Aerobic Aquatic Metabolism

- Represents metabolism in surface water
- Transformation of a pesticide in water and (some) sediment in the presence of oxygen(hence aerobic)
- Measures transformation of parent compound and formation and decline rates of transformation products
- Measures possible partitioning of parent compound and transformation products between water and sediment

# Anaerobic Aquatic Metabolism

- Represents suspended and bottom sediment in water
- Transformation of a pesticide in water and sediment in the absence of oxygen (hence anaerobic)
- Measures transformation of parent compound and formation and decline rates of transformation products
- Measures partitioning of parent compound and transformation products between water and sediment

# Laboratory Metabolism Studies (conducted in DARKNESS)

| | | Does the study contain? | | | | |
|---|---|---|---|---|---|---|
| **Test Guideline** | **Guideline Number** | **Soil** | **Water** | **Flooded soil** | **Oxygen atmosphere** | **Nitrogen atmosphere** |
| Aerobic soil | 162-1 835.4100 | Yes | Yes | No | Yes | No |
| Anaerobic soil | 162-2 835.4200 | Yes | Yes | No | No | Yes |
| Anaerobic aquatic | 162-3 835.4400 | Yes | Yes | Yes | No | Yes |
| Aerobic aquatic | 162-4 835.4300 | Yes | Yes | Yes | Yes | No |


# Soil Leaching/ Adsorption/Desorption Studies (835.1230/1240)

- Conducted on the parent compound
- Measures how far a pesticide can move into soil (leaching in soil)
- Measures binding with soil/ sediment(strongly binding, weakly binding)
- Measures sorption coefficients (Kd and Koc); higher the value, strongly binding)

# Non-Guideline Studies for Environmental Transport

- **Antifoulants** (For Pesticides used for boat and ship bottoms)
  - Used for parent
  - Non-guideline studies developed by ASTM (American Society for Testing Materials)
  - Measures the rate of pesticide release in water
- **Pressure Treated Wood Preservative (Pesticides)**
  - Non-Guideline studies developed by American Wood Preservers Association (AWPA E-11/12): Wood Blocks
  - Determining the Leachability of Wood Preservatives in Soil Contact (AWPA E20-08): Boards
  - Measure the amount of pesticide released into water and soil
- **Textiles and Plastics**
- **Ballast water** –No guideline or non-guideline studies

# Ballast Water

- “Fresh or salt water sometimes containing sediments held in tanks and cargo holds of ships to increase stability and maneuverability during transit”
- Water taken from one body of water and discharged or released into another water body can introduce invasive (non-native) species of aquatic life
- Ballast water must be treated prior to release from ship
- Estimated environmental concentration (EEC) of pesticide to lake or reservoir depends on the size of receiving water body.
- From EECs, risk quotients (RQs) are calculated to predict risk to aquatic species

# Why are WWTP Data Needed?

- To assess the potential effect of the antimicrobial on the microorganisms in the biological treatment processes of a WWTP.
- To assess the potential for the antimicrobial chemical to pass through the WWTP in the effluent to surface water where aquatic organisms and humans may be exposed. This is often referred to as a down the drain assessment (DtD)
- To provide more refined, less conservative, estimate of exposure.

# Biodegradation

## Definitions

- **Simple:** The destruction of organic compounds by microorganisms;
- **EPA**: A process by which microorganisms transform or alter (through metabolic or enzymatic action) the structure of chemicals introduced into the environment
- **USGS:** Transformation of a substance into new compounds through biochemical reactions or the actions of microorganisms such as bacteria.

# Sorption

- Sludge refers to the solids that settle out during the activated sludge treatment process.
- The Activated Sludge Sorption isotherm guideline
  - Procedure for measuring the extent to which a chemical compound distributes itself between activated sludge as the sorbent and water as the solvent.
  - If a chemical substance is sorbed to sludge biomass, it may be removed from WWTP systems along with other solids by clarification.
  - If a chemical substance is not sorbed, it will remain in the aqueous phase where it is subject to removal via biodegradation, chemical interactions, and/or volatilization.

# Eleven "New" Data Requirements

1. Photodegradation in soil
2. Soil residue dissipation
3. Activated sludge respiration inhibition (ASRI) test
4. Ready biodegradability study
5. Porous pot study
6. Simulation test – aerobic sewage treatment: activated sludge units
7. Simulation tests to assess the biodegradability of chemicals in discharged wastewater
8. Activated sludge sorption isotherm (ASSI) study
9. Developmental neurotoxicity
10. Immunotoxicity
11. Nature of the residue on surfaces.

"New" - a requirement that has never/rarely been required on a case-by-case basis, and has not been routinely considered during for the purpose of risk assessment

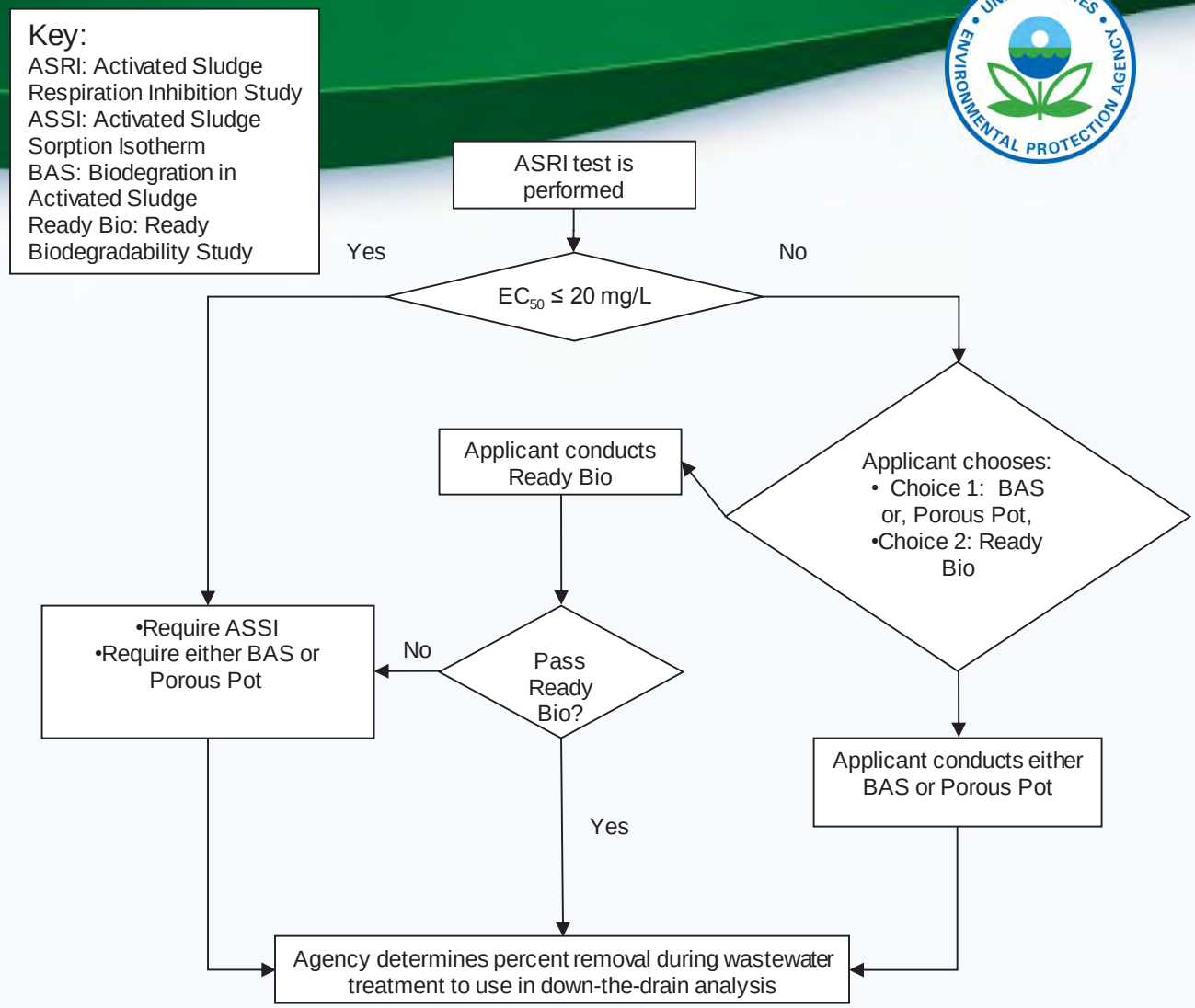
# WWTP Data Requirements

- Activated sludge respiration inhibition – determines toxicity of chemical substances to activated sludge microorganisms
- Biodegradation during wastewater treatment and information on biodegradates
  - Determines potential for biodegradation of chemical substance by activated sludge microorganisms
  - Biodegradation can be determined from a ready biodegradability test or a biodegradation in activated sludge simulation test
- Activated sludge sorption isotherm – used to determine removal from wastewater via sorption of chemical substance to biosolids (sludge)
- Consider rapid degradation of parent antimicrobial
- Formation of persistent degradates by hydrolysis and biodegradation must also be considered

Elements of the Assessment

# New WWTP Data Requirements

- Generally, always do three studies:
  - **Activated Sludge Respiration Inhibition**: to determine toxicity of antimicrobials to microorganisms in the activated sludge basin
  - **Tests for biodegradability** during wastewater treatment . Registrant chooses one of 4 – depends on toxicity to microorganisms)
  - **Activated Sludge Sorption Isotherm**: to determine what sticks to sludge and what stays in liquid


Key:
ASRI: Activated Sludge Respiration Inhibition Study
ASSI: Activated Sludge Sorption Isotherm
BAS: Biodegration in Activated Sludge
Ready Bio: Ready Biodegradability Study
ASRI test is performed
Yes
No
EC50 ≤ 20 mg/L
Applicant conducts Ready Bio
Applicant chooses:
• Choice 1: BAS or, Porous Pot,
•Choice 2: Ready Bio
•Require ASSI
•Require either BAS or Porous Pot
No
Pass Ready Bio?
Applicant conducts either BAS or Porous Pot
Yes
Agency determines percent removal during wastewater treatment to use in down-the-drain analysis

# WWTP Data Requirements-ASRI

## Why is an Activated Sludge Respiration Inhibition (ASRI) test required?

- To determine toxicity of a chemical substance to activated sludge microorganisms; toxicity can inhibit the ability of activated sludge microorganisms to remove organic matter and treat wastewater
- To determine whether a ready biodegradation test or a biodegradation simulation test is required
- If a chemical substance is too toxic to microorganisms, the performance of the ready biodegradation test will be compromised. The protocol for the ready biodegradation test states that chemical substances with $EC_{50}$ values of less than 20 mg/L are likely to pose serious problems.

# WWTP Biodegradation Tests

## What WWTP biodegradation tests are required?

Tests required are a ready biodegradation test (OCSPP 835.3110) or one of three simulation tests for biodegradation in activated sludge

Simulation tests include:

- Simulation Tests to Assess the Biodegradability of Chemicals Discharged in Wastewater (835.3280)
- Simulation Test – Aerobic Sewage Treatment: A. Activated Sludge Units (835.3240)
- Porous Pot Test (835.3220)

# Ready Biodegradability Test vs Biodegradation Simulation Test

- Ready biodegradability test
  - a solution of test substance is inoculated with microorganisms and incubated under aerobic conditions in the dark or in diffuse light.
  - A chemical passes the test if 70% of Dissolved Organic Carbon is removed in a 10-day window within the 28-day period of the test. For a respirometric test, the chemical must achieve 60% of the theoretical oxygen or theoretical carbon
- There are 6 different ready biodegradation tests:
  - DOC die-away
  - CO2 evolution (respirometric)
  - MITI (respirometric)
  - Closed bottle (respirometric)
  - Modified OECD screening
  - Manometric respirometry
- Biodegradation simulation test
  - Determines the elimination and primary and/or ultimate biodegradation of water-soluble organic substances by aerobic microorganisms in a continuously-operated test system simulating the activated sludge process. The method is designed to ascertain whether the chemical tested can be biodegraded within the limits imposed by typical WWTPs.

# WWTP Biodegradation Tests

How does one know whether a simulation test rather than a ready biodegradation test is required?

- If the result of the ASRI test is $EC_{50} \leq 20$ mg/L, a simulation test is required
- If the result of the ASRI test is $EC_{50} > 20$ mg/L, one can perform a ready biodegradation test or a simulation test; however, if the chemical fails the ready biodegradability test, a biodegradation simulation test is required

# WWTP Biodegradation Tests

## When is a WWTP biodegradation test not required?

- When a chemical substance is classified as a metal
- When a chemical is relatively volatile, but not hydrophobic
- When a chemical is highly reactive
- When both the parent chemical and all of its transformation/degradation products have half-lives of less than 3 hours
- When none of the registered or proposed product uses would result in transport of the parent and its transformation/degradation products to a wastewater treatment plant

# WWTP Activated Sludge Sorption Isotherm (ASSI) Test

Under what circumstances is an ASSI test not required?

- If an antimicrobial is relatively volatile, but not hydrophobic
- If an antimicrobial is highly reactive
- If the log $K_{ow}$ < 3.0

# WWTP Activated Sludge Sorption Isotherm (ASSI) Test

What criteria trigger the requirement for an ASSI test?

- The antimicrobial is a metal
- The log $K_{ow} \geq 3.0$
- The antimicrobial is positively charged or polycationic
- The $EC_{50}$ in the ASRI test is ≤ 20 mg/L
- The $EC_{50}$ in the ASRI test is > 20 mg/L and the antimicrobial fails the ready biodegradability test

# Summary

- Data from environmental fate studies are not intended to increase economic burden; they are intended to provide better and less conservative estimates of exposure
- Only data that are needed to assess risk are required
- § 158.2280 Environmental Fate Data Requirements table contains test notes that provide specific information that can be considered with regard to chemical and use characteristics to determine when fate studies are and are not needed.