

CHARACTERIZING AIR EMISSIONS FROM WASTEWATER FACILITIES

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Odors and Air Pollutants

2016

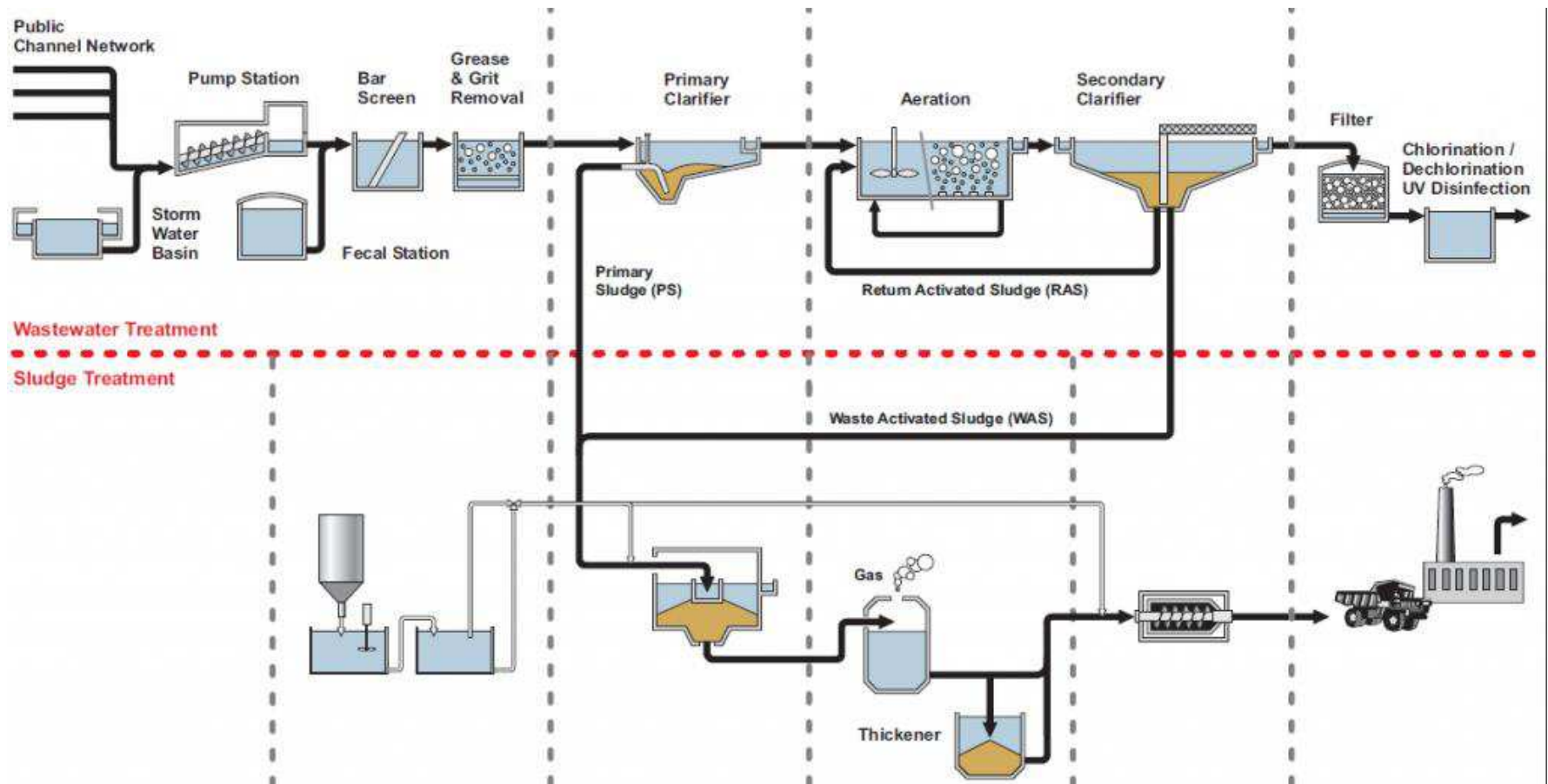


Agenda

- Overview – air emissions in wastewater treatment
- Sources of emissions
- Measurement & Reporting of emissions
- Role of Fate & Transport models in characterizing Air Emissions
- Conclusion

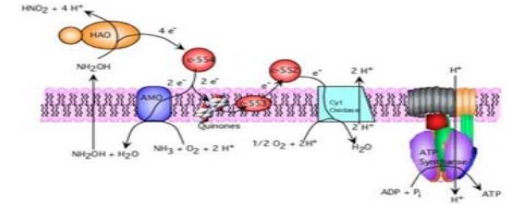
Wastewater Treatment

The Activated Sludge Process



Air Pollutants & Odors

Sources in wastewater treatment



Generated In-situ



- THMs from Cl₂ disinfection
- Reduced Sulfur Compounds

O₂ – Aerobic → CO₂

NO₃ – Anoxic → N₂

SO₄ – Anaerobic → H₂S

In Wastewater influent



Odors – Mercaptans, H₂S
VOCs – Benzene, Toluene, etc.
HAPs

Air Pollution Regulations Through the Years

The Air Pollution Control Act of 1955

- First federal air pollution legislation
- Funded research on scope and sources of air pollution

Clean Air Act of 1963

- Authorized a national program to address air pollution
- Authorized research into techniques to minimize air pollution

Air Quality Act of 1967

- Enforcement procedures involving interstate transport of pollutants
- Expanded research activities

Clean Air Act of 1970

- Established National Ambient Air Quality Standards (NAAQS)
- Established requirements for State Implementation Plans
- Establishment of New Source Performance Standards for stationary sources
- **Establishment of National Emission Standards for Hazardous Air Pollutants**
- Authorized control of motor vehicle emissions

1977 Amendments to the Clean Air Act of 1970

- Authorized provisions related to prevention of significant deterioration
- Authorized provisions relating to non-attainment areas

1990 Amendments to the Clean Air Act of 1970

- Authorized programs for acid deposition control
- **Authorized controls for 189 toxic pollutants, including those previously regulated by the national emission standards for hazardous air pollutants (HAPs)**
- **Established permit program requirements**
- Expanded provisions concerning NAAQS

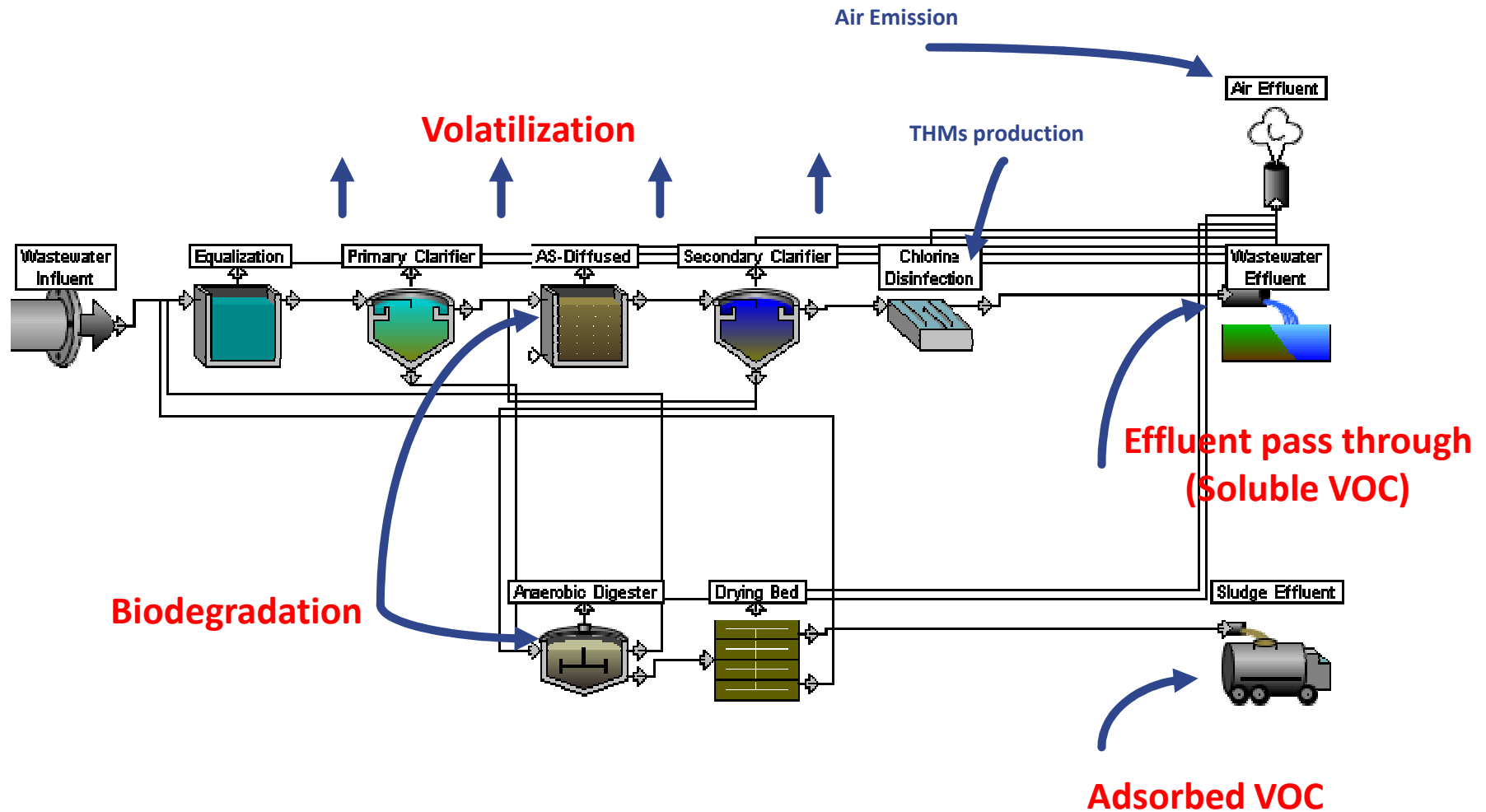


- What happens to odors & HAPs in conveyance & WWTP (Fate & Transport)
- What happens to HAPs that are emitted into the air at the treatment plant (Dispersion)?

Fate & Transport models developed in response to 1990 CAA Amendments

Contaminant Fate & Transport in Wastewater Treatment

How are they removed?



What are Emission Sources?

- Wherever energy is transferred to wastewater (wherever turbulence is created)
 - Gravity (waterfalls, weirs)
 - Mixers
 - Surface Aerators
 - Diffusers
- Wherever air streams with low concentrations of VOCs are in contact with VOC laden liquids

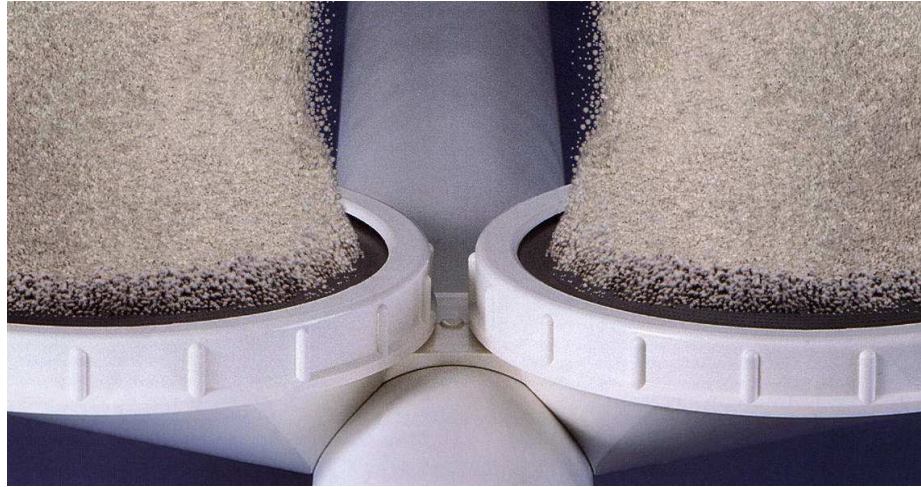
Activated Sludge Aeration

Mechanical Aeration



- Extreme turbulence causes VOC stripping and surface renewal

Diffused Aeration



- Only about 10-20% of O_2 is dissolved
- i.e., only 2-4% of influent gas @ 21% O_2 is dissolved
- ~96%-98% vent gas strips VOCs and odors!

Clarifiers

Surface



- Large surface area enhances VOC release

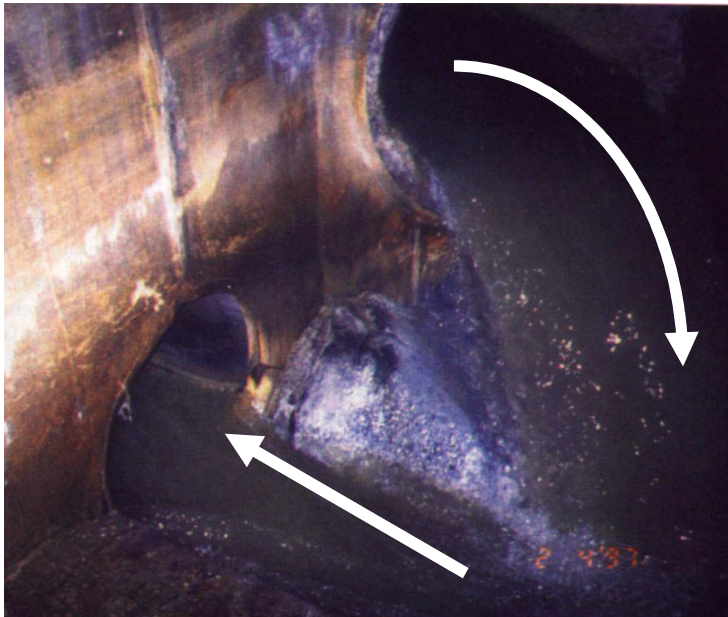
Weirs



- Note foam in the trough due to air entrainment

Emissions from Drop Structures & Ponds

Drop Structure



- A drop structure with process flow flowing into an existing process stream

Equalization Ponds



- Wind passing over large wastewater surface areas results in high surface volatilization rates

Emissions Estimation Methods

Direct Methods

Direct Measurement of Off-gas

- For enclosed headspaces, pipe flows, etc.
- Analyze concentration in off-gas flow (C_g)
- Measure off-gas flow rate (Q_g)
- Emission rate = $C_g * Q_g$

Measurement from Open Surfaces

- For open, non-confined surfaces (e.g. aeration tanks)
- Use floating flux chambers
- Trap and analyze emissions from surface area enclosed by chamber
- Measure gas flow through chamber
- Emission rate = $C_g * Q_g$

Indirect Methods

Emission Factors (EFs)

- Often based on some unit of production (e.g. lb of product per day) or WWTP operation (e.g. flow)
- Mass emitted = EF * mass production rate
- Accuracy is not that great; requires much historical evidence

Mathematical Modeling

- Main EPA approved models are BASTE, TOXCHEM™ and WATER9 (EPA)
- Based on mass balances, kinetic rate expressions and empirically-derived relationships

Measurement from Covered Tanks



- Measure off-gas flow rate (Q_g)
- Emission rate = $C_g * Q_g$

Measurement from Open Surfaces

Floating Flux Chamber

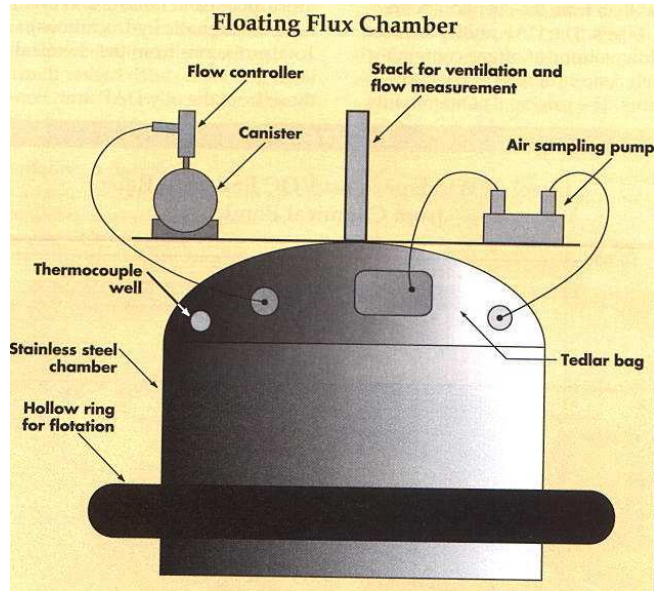


Fig D. Measuring Emissions from a Refinery Aerated Lagoon



Fig G. Municipal Wastewater Treatment

Direct Measurement of Air Emissions is Very Challenging

Indirect Estimation Methods

Emission Factors (EFs)

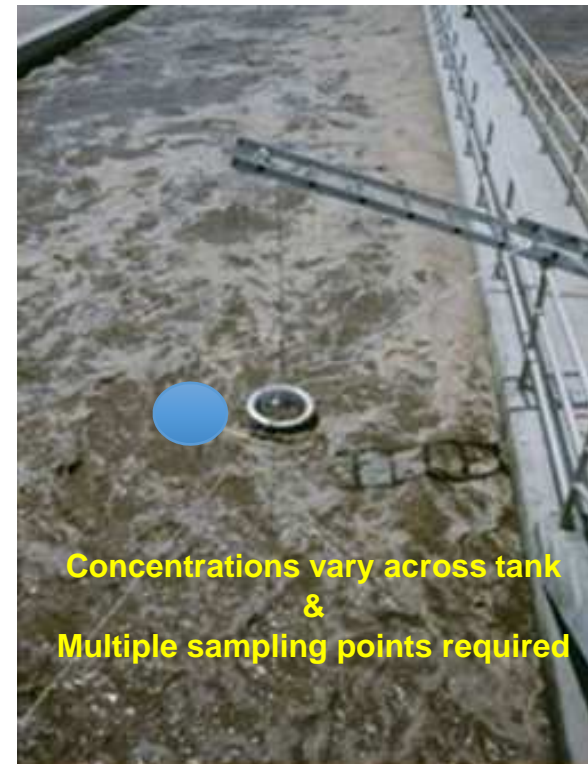
- Often based on some unit of production (e.g. lb of product per day) or WWTP operation (e.g. flow)
- Mass emitted = EF * mass production rate
- Accuracy is not that great; requires much historical evidence

Mathematical Modeling

- EPA specifies applicable modeling methods in 40 CFR Part 63
- Two main models are TOXCHEM™ and WATER 9 (EPA)
- Based on mass balances, kinetic rate expressions and empirically-derived relationships

Reasons for Modeling

- Representative samples may be hard to collect
- Field staff may lack knowledge or resources for optimum sampling
- Measurements impacted by lots of variables – wind speed, throughput (Hi/Low flow), etc.
- Applicable to facilities in upgrade or design

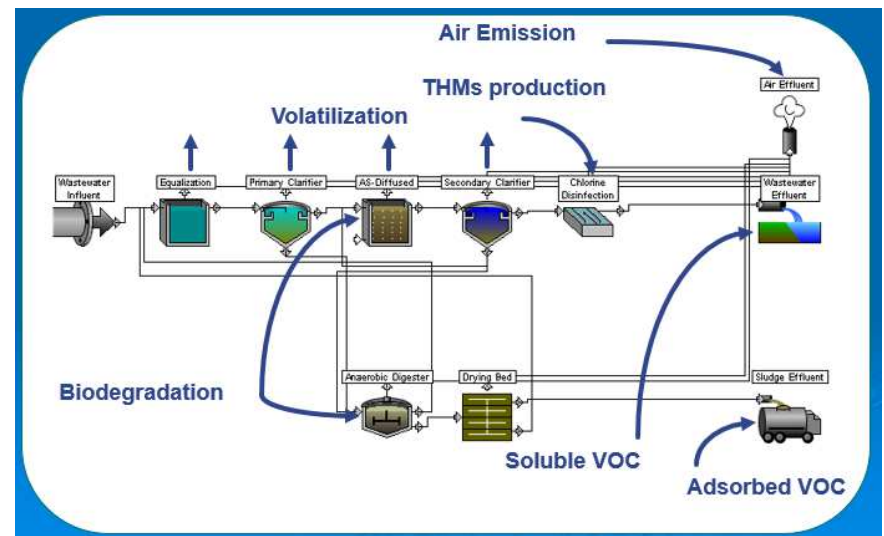


Modeling offers a robust, regulatory approved means of determining pollutant fate

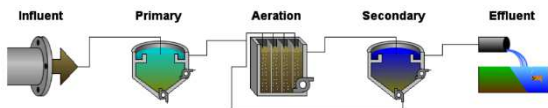
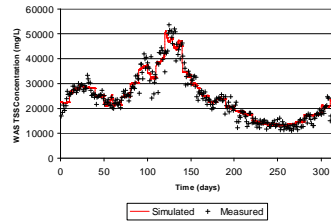


Contaminant Fate & Transport Model

- Estimates fate and emission rates of organic compounds and metals from collection and treatment system components
- Used since 1991, +840 compounds & metals
- Specified in regulations (CAAA, SARA – 40 CFR, Part 63)
- Customizable (processes, compounds, parameters)
- Applications
 - Contaminant fate
 - Technology evaluation
 - Parameter estimation / validation



How Models are Used



$$\frac{dx_l}{dt} = \frac{\mu_m S_e}{K_s + S_e} x_l - k_d x_l$$

- Hydraulic model
- Biological model
- Aeration model
- Equilibrium chemistry
- Transport
- Mechanical & Thermal effects

Create Model

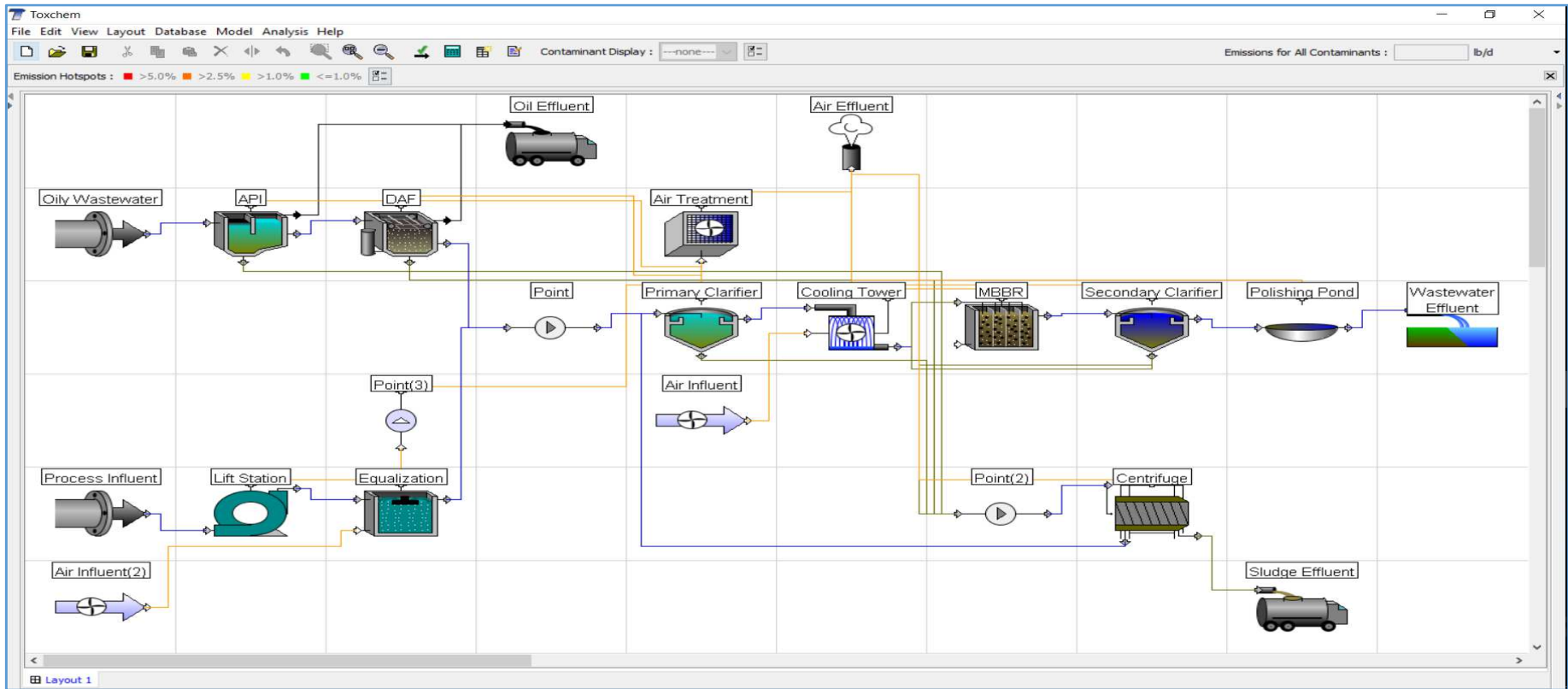
Calibrate to Known Performance

Generate Compliance Reports

Sensitivity analyses

Compare, Evaluate & Troubleshoot

Characterizing Emissions With Toxchem



- Multiple influent streams
- 13 contaminants across both streams
- Several unique process treatment steps

Characterizing Emissions With Toxchem

The image displays six screenshots of software interfaces for characterizing emissions with Toxchem:

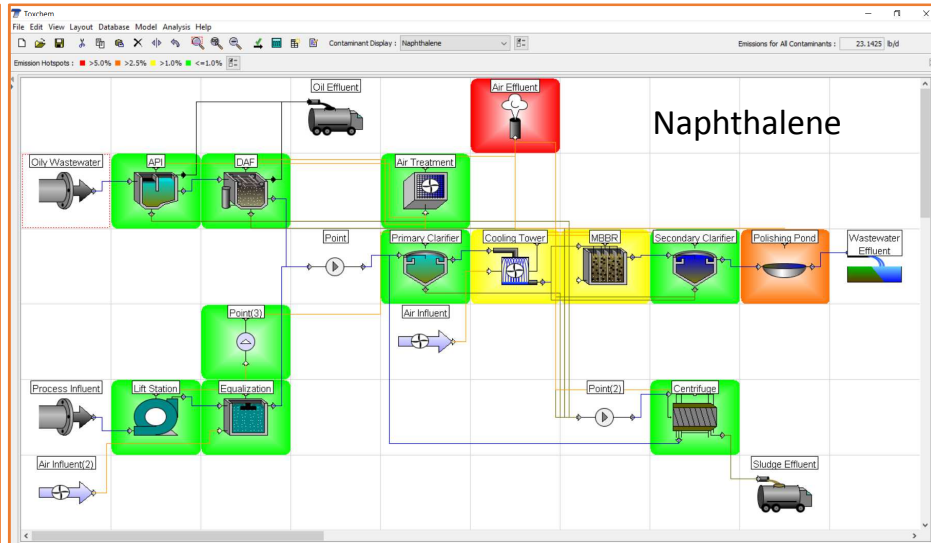
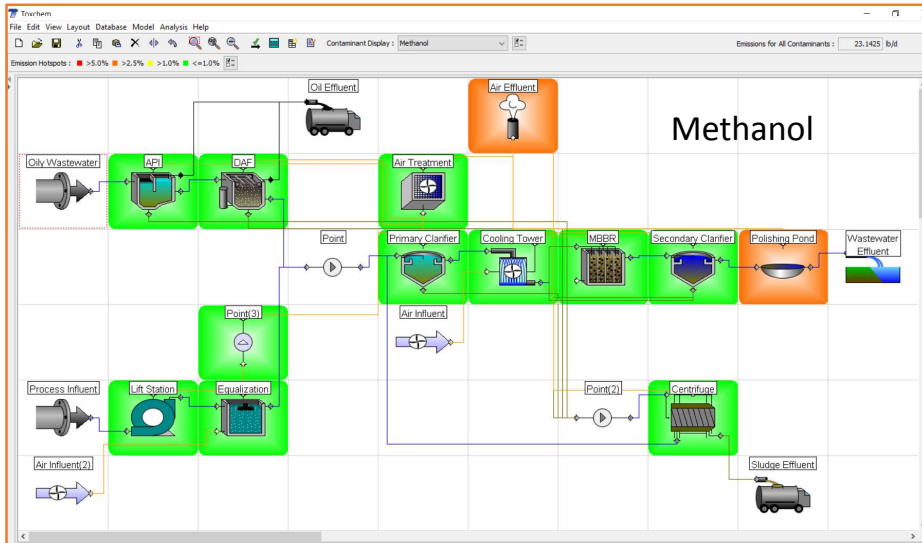
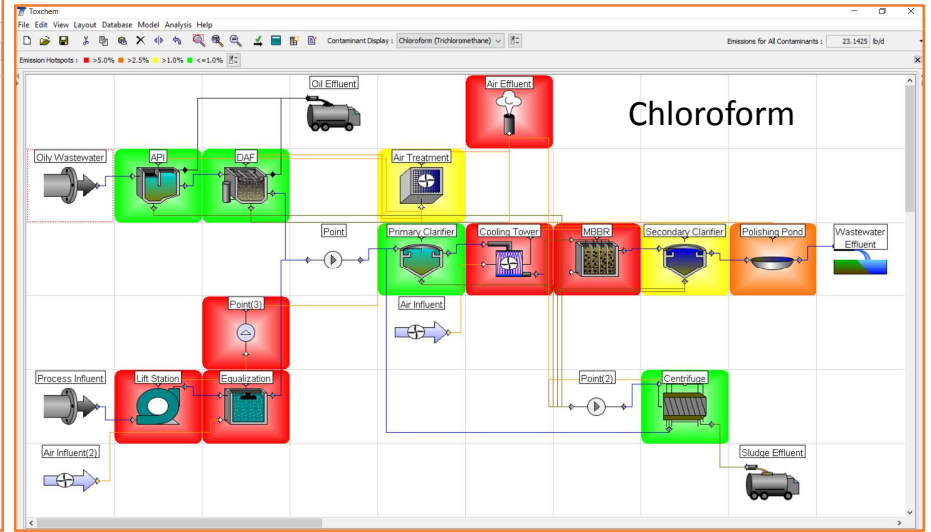
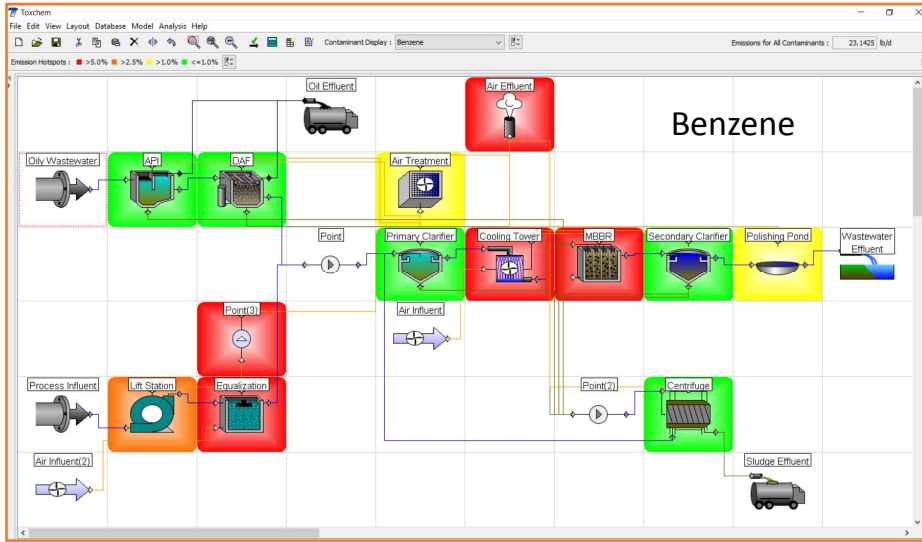
- Oily Wastewater (Contaminants):** Shows a list of contaminants with their concentrations in ug/L. Contaminants include 1,2-Dimethylnaphthalene, Acenaphthene, Benzene, Benzo(A)Pyrene, Toluene, Hexane(+), Xylene,P- (1,4-Xylene), and Naphthalene, all set to 100.0 ug/L.
- Oily Wastewater (Flow Split):** Shows flow rate parameters: Flow Rate (30000.0 m3/d), Suspended Solids (500.0 mg/L), VSS to SS Ratio (75.0 %), Wastewater DOC (0.0 mg/L), Oil/Grease Concentration (500.0 mg/L), and Temperature (30.0 deg C).
- Emission Hotspot Setup:** Shows options for base output (percent emissions or loading emissions) and thresholds for high, medium, and low level emitters. High level emitters are greater than 5.0 %, medium level emitters are greater than 2.5 %, and low level emitters are greater than 1.0 %.
- Process Influent (Contaminants):** Shows a list of contaminants with their concentrations in ug/L. Contaminants include Acetone, Benzene, Chloroform (Trichloromethane), Dichlorobenzene, 1,4-, and Methanol, all set to 100.0 ug/L.
- Process Influent (Flow Split):** Shows flow rate parameters: Flow Rate (20000.0 m3/d), Suspended Solids (200.0 mg/L), VSS to SS Ratio (75.0 %), Wastewater DOC (0.0 mg/L), Oil/Grease Concentration (0.0 mg/L), and Temperature (25.0 deg C).
- API (Advanced):** Shows various parameters for API: Liquid Depth (2.4 m), Surface Area (1500.0 m2), Weir Length (100.0 m), Waterfall Height (0.2 m), SS Removal Efficiency (50.0 %), Oil Removal Efficiency (80.0 %), Sludge SS Concentration (10000.0 mg/L), Flow Rate of Recovered Oil Stream (0.132085 MGD(US)), Covered (checked), Ventilation Rate (100.0 m3/hr), and Local pH value (7.0).

- Each unit process can be specified
- +840 chemicals and metals are available
- Custom data can be input as well

Database Details

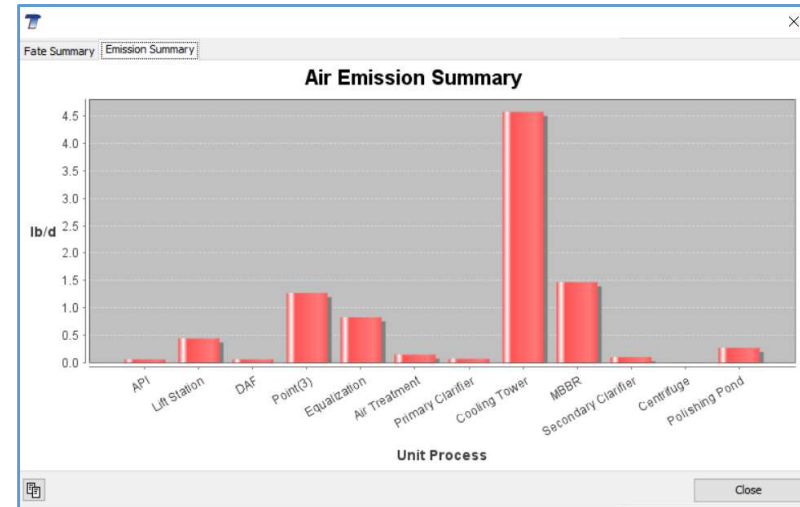
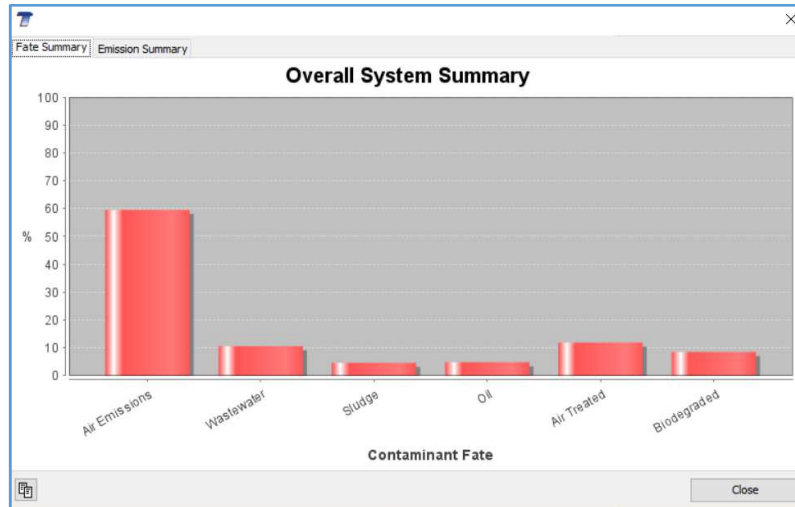
The screenshot displays the 'Organic Chemical Database' application window. On the left, the 'Organic Chemical List' is shown with a filter set to 'All'. A search bar is present with 'Find' and 'Search by CAS #' buttons. The list includes various polycyclic aromatic hydrocarbons and other compounds, with '1,2-Dimethylnaphthalene' selected. On the right, the 'Selected Organic Chemical Details' for '1,2-Dimethylnaphthalene' are shown under the 'Biodegradation' tab. The 'Sludge Process' section includes an unchecked checkbox for 'Anaerobic Sludge Biodegradation Rate @ 35 C' and a text box for 'Aerobic Biodegradation Rate (Kb) @ 20 C' containing the value '0.009283'. The 'Liquid Process' section includes a text box for 'Aerobic Biodegradation Rate (Kb) @ 20 C' with '0.009283', an unchecked checkbox for 'Half Saturation Constant (Ks)', and text boxes for 'Anoxic Reduction Factor (fanox)' (0.8) and 'Anaerobic Reduction Factor (fana)' (0.1). 'Accept' and 'Cancel' buttons are at the bottom right.

Process	Parameter	Value	Units
Sludge Process	Anaerobic Sludge Biodegradation Rate @ 35 C	<input type="checkbox"/>	L/(mg.hr)
	Aerobic Biodegradation Rate (Kb) @ 20 C	0.009283	L/(mg.hr)
Liquid Process	Aerobic Biodegradation Rate (Kb) @ 20 C	0.009283	L/(mg.hr)
	Half Saturation Constant (Ks)	<input type="checkbox"/>	mg/L
	Anoxic Reduction Factor (fanox)	0.8	
	Anaerobic Reduction Factor (fana)	0.1	

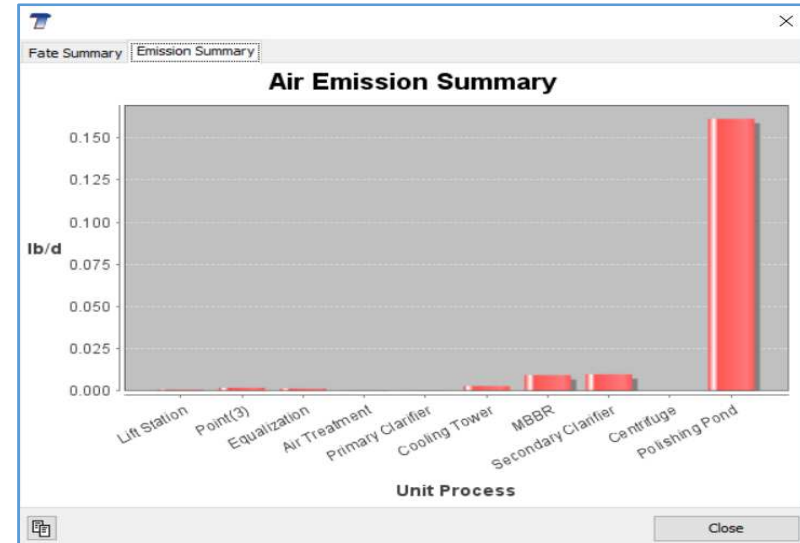
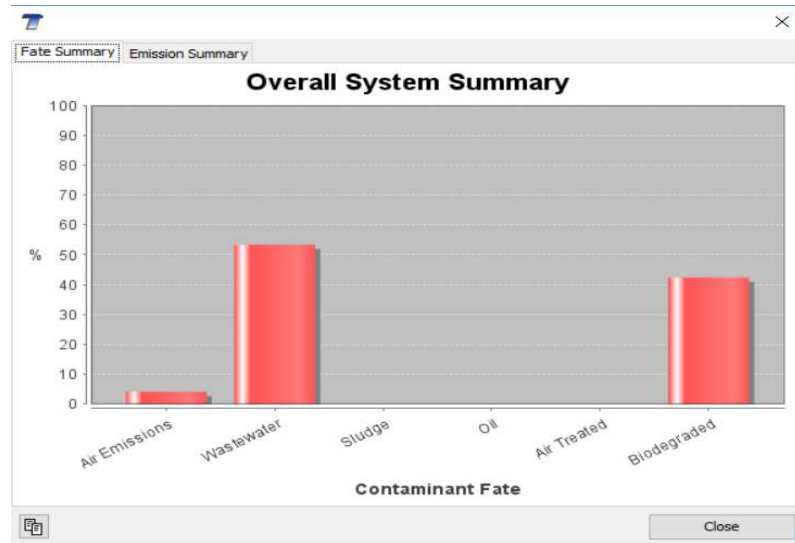


Characterizing contaminant Fate

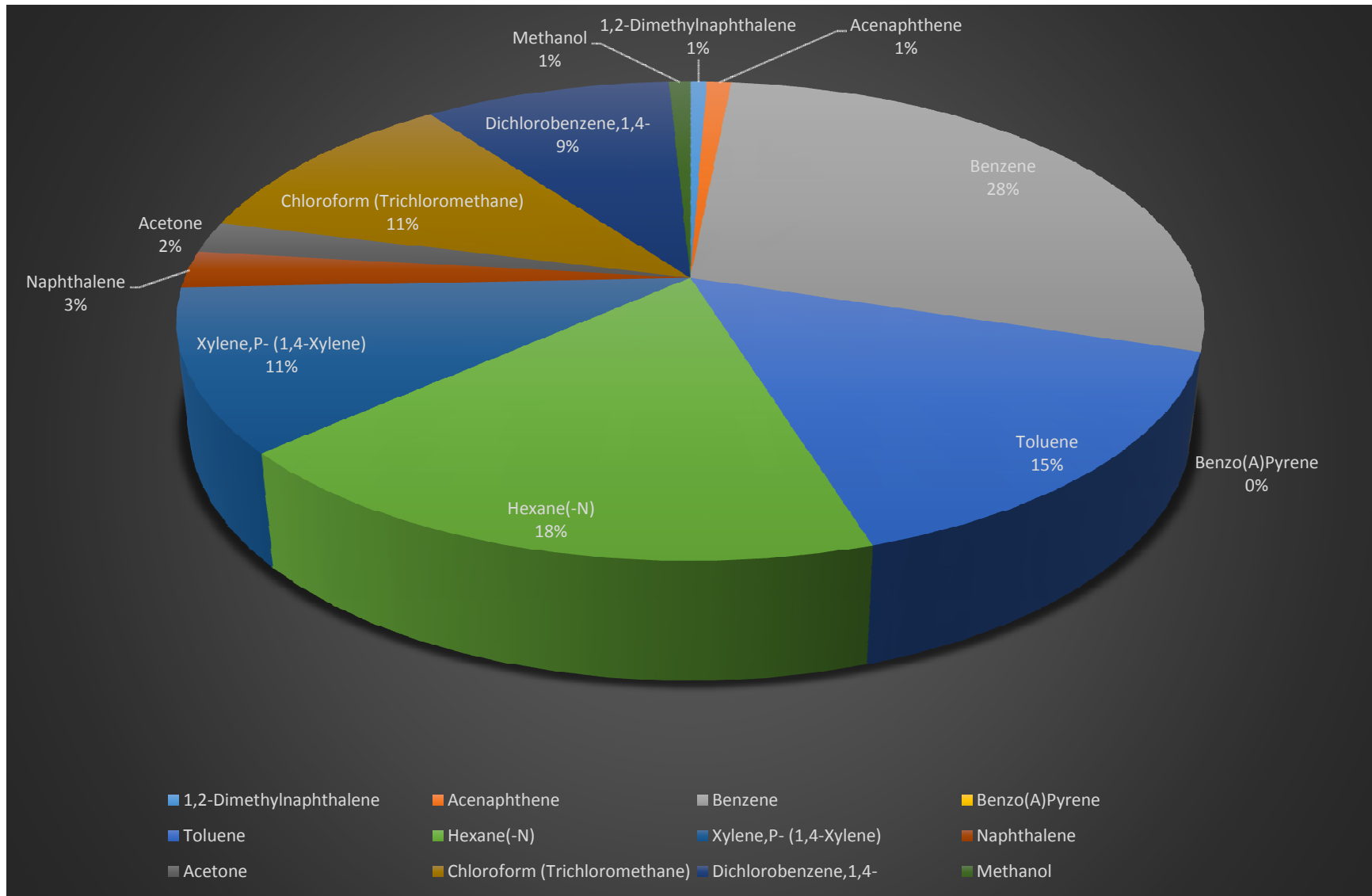
Benzene



Methanol

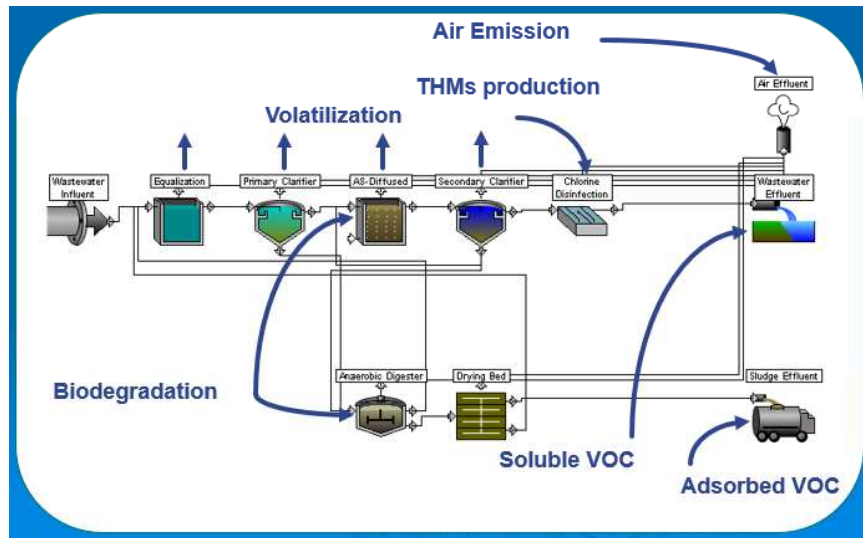


Total Air Emissions Summary

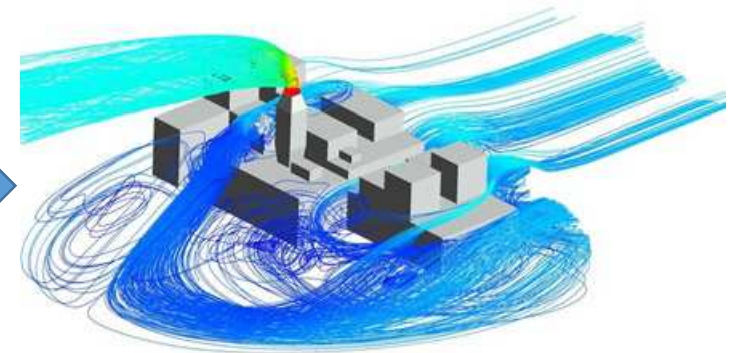


Relationship between Fate & Transport Models and Dispersion Models

Fate & Transport models: What happens to Odor & air emissions in Conveyance systems and treatment Plant (Water 9, Toxchem™)



Dispersion Model: How far do the emissions carry? (AERMOD, CALPUFF)



Most accurate Fate & Transport model

Conclusion

- Odors and VOCs are generated / released in the wastewater treatment process
- Process models offer a robust approach for characterizing emissions
 - Have regulatory approval (40 CFR Part 63)
 - Comprehensively cover all aspects of wastewater treatment
 - Can be calibrated to site specifics
- Additional benefits of modeling
 - Incorporate emission mitigation into process design
 - Enable sensitivity analyses
 - Troubleshooting – e.g., odor & emission sources & concentrations
 - Can be readily integrated with dispersion models

Questions

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Factors Affecting Air Emissions

- **Waste characteristics** – flow rate, temperature, chemical composition, others (suspended solids, oils)
- **Chemical compound properties** – Henry's coefficient (volatility), molecular weight, density, partition parameters. Biodegradation rates
- **Process unit parameters** – physical dimensions, process parameters, covered or open processes, air flow rates, aerator power input, sludge characteristics
- **Site & ambient conditions** – temperature, wind speed, elevation

Clean Air Act – 11 Titles

- Title I – attainment & maintenance of NAAQS*
- Title III – Air Toxics Control
- Title IV – Acid Rain Control
- Title V – Permits & Reporting
- Title VI – Stratospheric Ozone Protection
- Tile VII - Enforcement

Regulated Air Pollutants

- Six criteria pollutants from 1963 CAA (SO, NO_x, CO, Pb, O₃, Pm)
- VOCs
- NSPS – H₂S, Reduced Sulfur Compounds, total reduced sulfur, sulfuric acid mist, dioxin/furan, fluorides and HCl
- 188 Hazardous Air Pollutants (HAPs)

* NAAQS - National Ambient Air Quality Standards

Emission Factors

U.S. ENVIRONMENTAL PROTECTION AGENCY

Technology Transfer Network
Clearinghouse for Inventories & Emissions Factors

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Emission Estimation Protocol for Petroleum Refineries

Emission Estimation Protocol for Petroleum Refineries - Version 3.0 (PDF 2,956K) posted April 20, 2015.

Questions
 For questions about the guidance document or the tool, contact Brenda Shine at shine.brenda@epa.gov

Background Documentation
 These documents have been posted for information purposes only.

- [Refinery wastewater emissions tool spreadsheet - March 2011](#) (XLSX 207K)
- [Petroleum Refinery Source Characterization and Emission Model for Residual Risk Assessment](#) (PDF 523K). Prepared for U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC. EPA Contract No. 68-D6-0014. July 2, 2002.
- [Petroleum Refineries: Background Information for Proposed Standards](#) (PDF 5.7M). Background information on the proposed petroleum refinery MACT standards. EPA EPA-453/R-98-003, June 1998.

Office of Air Quality Planning & Standards | Technology Transfer Network | Clearinghouse for Inventories & Emissions Factors

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<http://www3.epa.gov/ttn/chief/efpac/protocol/index.html>
 Print As Is

Last updated on 9/10/2015

REFINERY WASTEWATER EMISSION TOOL: ICR VERSION 2.1 (RWETv2.1)

Please enter your Facility ID, Facility Name, and WWTS ID for the information provided in:

Facility ID No.:

Facility Name:

WWTS ID No.:

Form Approved OMB Control No. 2060-Approved Engineer

The Refinery Wastewater Emissions Tool Version 2.1 (RWET) is an Excel-based model designed to help regulated facilities estimate air emissions from wastewater collection and treatment systems. Separate sheets in RWET represent individual components in a typical wastewater treatment system and can estimate emissions for that particular unit. Effluent concentrations from a particular component can then be used as inputs for the next downstream collection or treatment unit. The calculations are primarily based on those presented in EPA AP-42 but also include updates deemed more accurate in the literature. The equations are presented in Appendix B of the emission protocol document.

Each sheet is set-up with a series of **critical inputs**, **constants/variables** with default values, and **outputs**. The following procedure should be used to reliably use RWET:

1. Determine the critical inputs of the unit listed on the corresponding sheet of RWET and record them on appropriate sheet.
2. Determine the influent concentrations of the pollutants of interest and input them into the model.
3. Review the default values of the variables and constants and make site-specific adjustments if necessary.
4. Review the chemical properties sheet and make any site-specific adjustments if necessary.
5. Record the air emissions for reporting and copy the pollutant effluent concentrations as inputs to the next downstream unit.
6. Repeat this process for the next downstream unit.

Introduction | Sheet1 | POTW Discharge | Wastewater Collection System | Weir | Oil-Water Separators

- Often based on some unit of production (e.g. lb of product per day) or WWTP operation (e.g. flow)
- Mass emitted = EF * mass production rate
- Accuracy is not that great; requires much historical evidence

<http://www3.epa.gov/ttn/chief/efpac/protocol/index.html>