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Enhancing Environmental Monitoring Using Total Organic Carbon (TOC)

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Outline of the Presentation

- Introduction
  - Measuring Organic Matter
  - BOD5 Test Characteristics
  - Substituting the BOD5 Test
  - Monitoring and Control in Wastewater Treatment
- Example: City of Santa Cruz, CA
- Research Project
  - Introduction
  - Sampling and Analysis
  - Preliminary Data

Introduction

- **Proteins** (40-60%)
- **Carbohydrates** (25-50%)
- **Oils and Fats** (8-12%)
- **Synthetic Organic Molecules**

Biochemical Oxygen Demand (BOD)

OXYGEN Consumption by Mixed Bacterial Culture

Chemical Oxygen Demand (COD)

OXIDANT Consumption

Total Organic Carbon (TOC)

CARBON DIOXIDE Generated from Complete Combustion

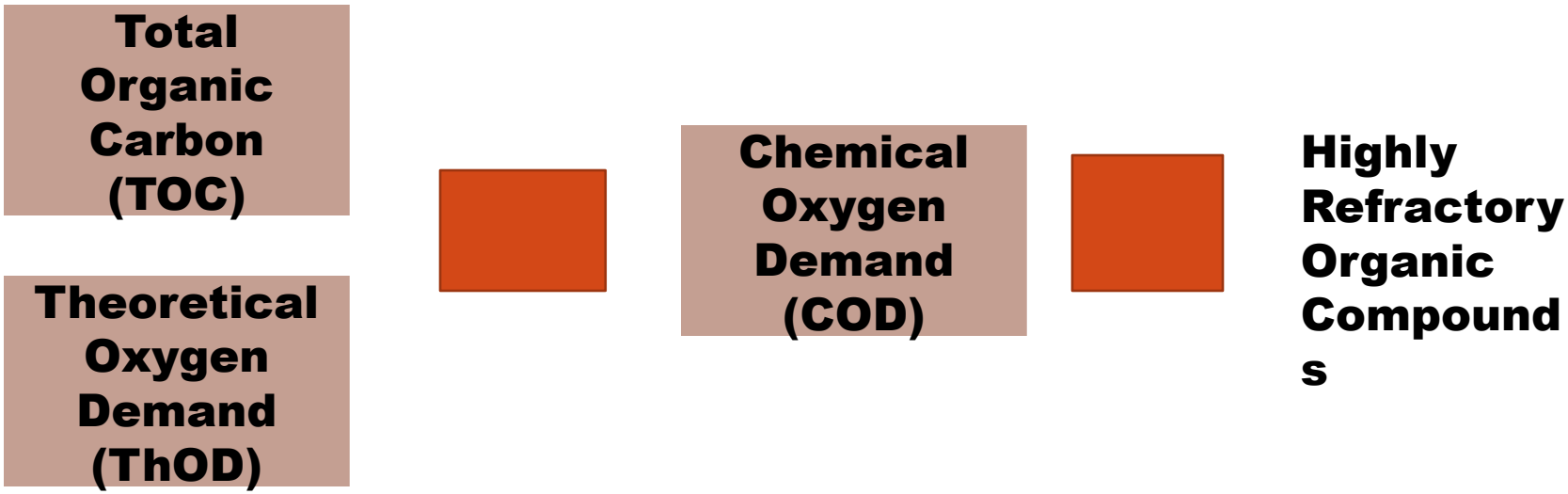
Theoretical Oxygen Demand (ThOD)

STOICHIOMETRIC OXYGEN Demand

Gross concentrations!

Introduction: Measuring Organic Matter

What is the Formal Relationship Between These Fractions??



Introduction: Biochemical Oxygen Demand

- BOD Dilution Test
- Several dilutions of sample
- Incubation bottles (300mL)=diluted sample + microorganism seed + nutrient solution
- Incubation at 20°C
- Measurement of dissolved oxygen every 24h period

Introduction: Chemical Oxygen Demand

- Standard dichromate test
- Heat under total reflux conditions a measured sample with known excess potassium dichromate in the presence of sulfuric acid
- Silver sulfate catalyst
- At the end of test, remaining dichromate determined by titration

$$C_nH_aO_bN_c + dCr_2O_7^{2-} + (8d + c)H^+ \rightarrow nCO_2 + \frac{a + 8d - 3c}{2}H_2O + cNH_4^+ + 2dCr^{3+}$$

Introduction: Total Organic Carbon

- Fundamental operation principle
  - Combustion of organic matter to CO2 and H2O
  - CO2 sensor determines carbon concentration
  - Method needed to separate inorganic carbon (IC) from total carbon (TC)
- High temperature catalytic combustion
- Moderate temperature UV-persulfate combustion
- Acidification of sample to convert IC to CO2 and

Introduction: The BOD5 Test

- Since adopted in 1936 (American Public Health Association Standard Methods Committee):

Introduction: The BOD5 Test

Introduction: Substituting the BOD5 Test

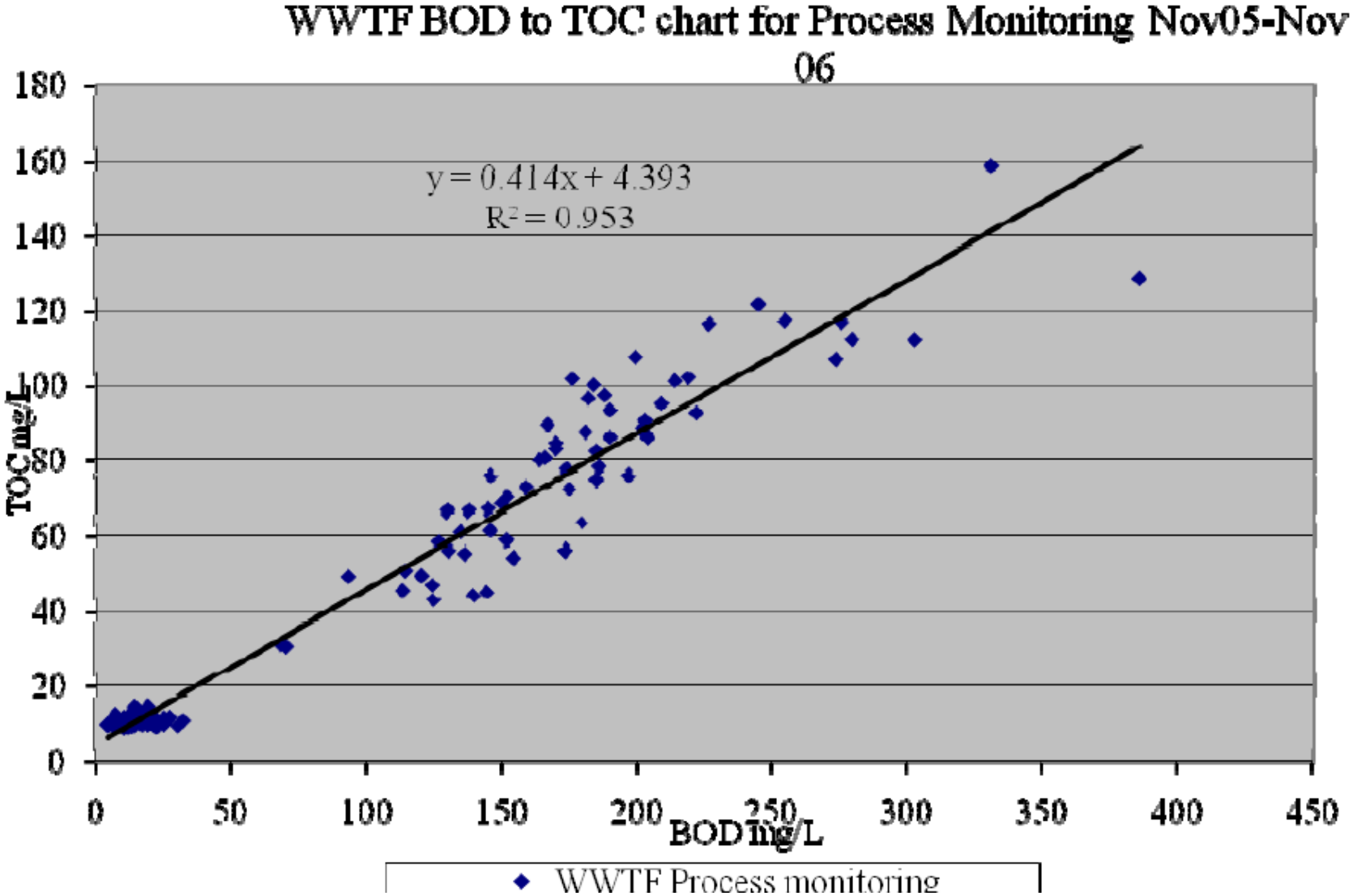
Analysis	BOD	COD	TOC
Labor Time	1.5 hour	15 minutes	30 minutes
Labor Cost	$45.00	$7.50	$15.00
Chemical & Glassware Cost	~$0.00	$6.00	$2.50
Total Cost	$45.00	$13.50	$17.50

Introduction: Monitoring and Control in Wastewater Treatment

Example: City of Santa Cruz WWTP

- Federal regulation 40CFR133.104 (b): ‘Chemical oxygen demand (COD) or total organic carbon (TOC) may be substituted for BOD5 when a long-term BOD:COD or BOD:TOC correlation has been demonstrated’.
- Santa Cruz WWTP decided to pursue a permit change:
  - Analytical considerations; difficulties in maintaining the 20°C required for the test.
  - Resource considerations; $100,000 required to retrofit the laboratory.

Example: City of Santa Cruz WWTP



(Babatola and Xu, 2009)

Example: City of Santa Cruz WWTP

Table F-4. Secondary Treatment Requirements

Parameter	Effluent Limitation		
	30-Day Avg	7-Day Avg	Percent Removal [1]
BOD_5	30 mg/L	45 mg/L	85
$CBOD_5$ [1]	25 mg/L	40 mg/L	85
TSS	30 mg/L	45 mg/L	85
pH	6.	9.0	---

Parameter	30-Day Avg	7-Day Avg	Percent Removal
TOC	**16.8 mg/L**	**23 mg/L**	**Substitute from eq.**

Research Project: Introduction

- Instrumentation Testing Association (ITA) and Illinois Institute of Technology (IIT) partnered to develop long-term correlations of BOD5 and COD to TOC
- Objectives:
  1. Demonstrate a long-term correlation of BOD and COD to TOC
  2. Evaluate the performance of online TOC analyzers
  3. Develop a step-by-step guide of protocol and procedures to be used as a tool for modification of permits

Research Project: Introduction

- WWTPs representative of different flows, treatment technologies and watershed ecosystems
- First study : Oceanside Water Pollution Control

Parameter	Primary Effluent		Final Effluent	
	Range (mg/L)	Average (mg/L)	Range (mg/L)	Average (mg/L)
Total Suspending Solids (TSS)	278-520	368	9-17	12.5
Biological Oxygen Demand (BOD)	ND	ND	9-25	16.9
Total Organic Carbon (TOC)	ND	ND	ND	ND
Chemical Oxygen Demand (COD)	583-943	736	44-60	50
pH	7.6-8.1	8.0	6.6-6.8	6.7

	Weather Type	Flow (MGD)
Average Daily	Dry	14
Design Average Daily	Dry	21
Design Peak Hourly	Dry	43
Design Peak Daily	Dry	24
Design Peak Daily	Wet	43
Design Peak Hydraulic - Secondary bypass	Wet	65

Research Project: Sampling and Analysis

- Sampling
  - 24-hour composite samples from primary and final effluent once a week
  - Each sample filtered through 0.45µm filter: two types of sample, unfiltered (‘total’) and filtered (‘dissolved’)
- BOD5 analysis (OSP)
- COD analysis (OSP)
- TOC analysis
  - Sample preservation in OSP
  - Triplicates of each of 4 samples sent to

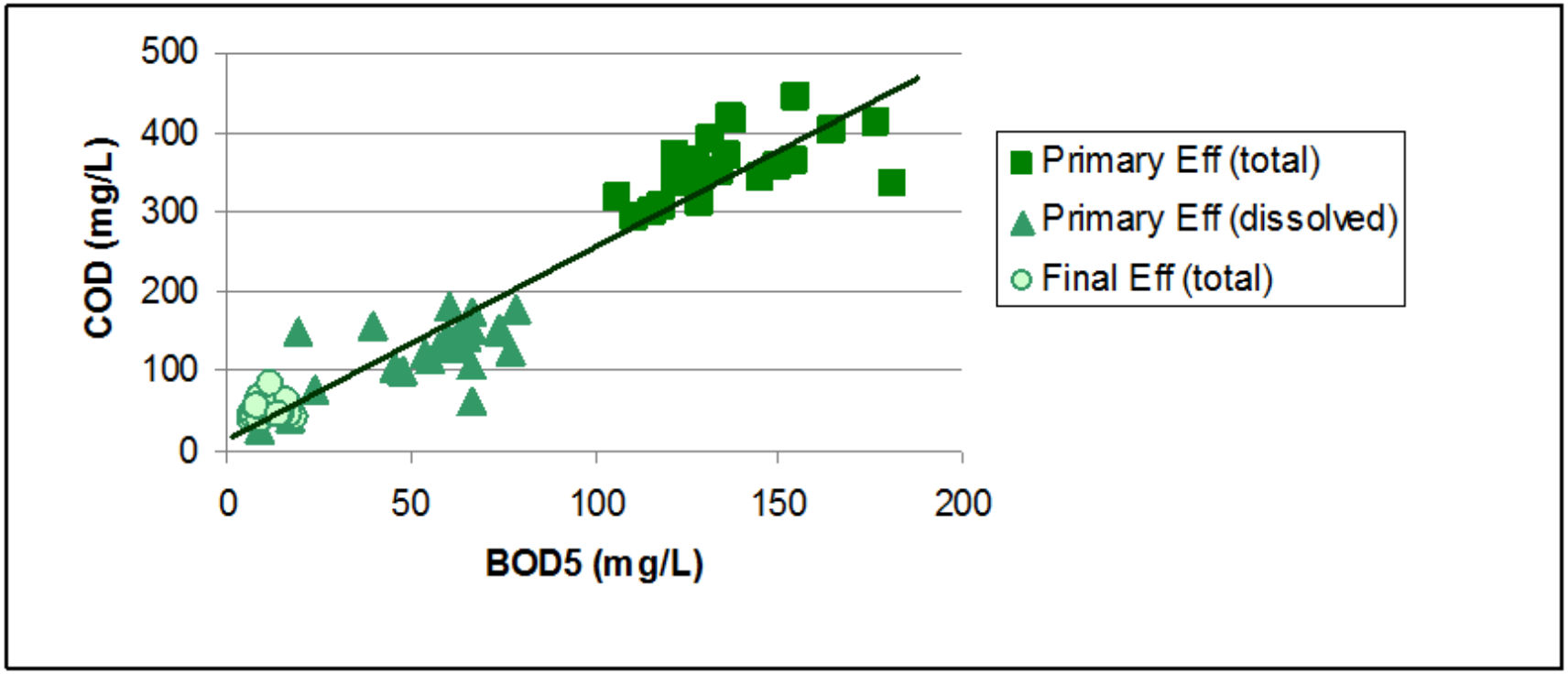
Research Project: TOC Analysis Discrepancies

- ‘Total’ samples due to filter-effect of sampling syringe
- ‘Dissolved’ samples not due to different TOC analysis equipment

	Standard solution mg/L)	[TOC] (mg/L)	
		SEP	IIT
Solution A	80	81.5	74.3
Solution B	30	28.9	28.1

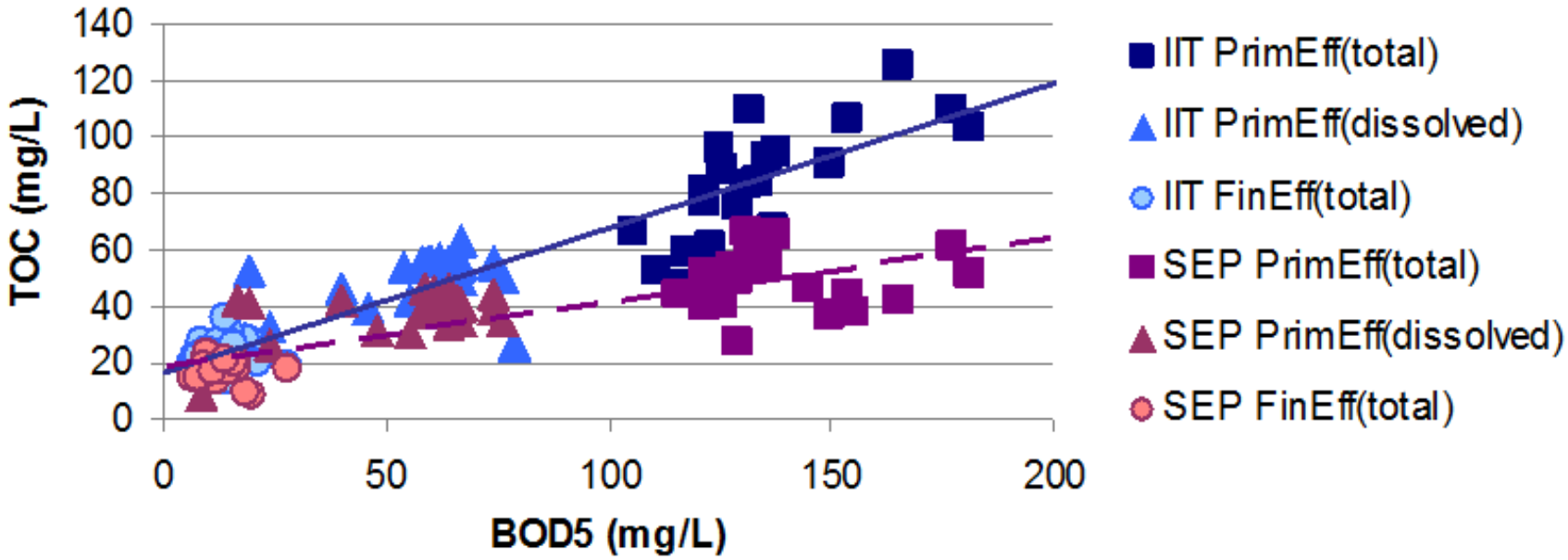
- Differences probably due to sample preservation method

Research Project: COD Data



Equation #	Sample Type	Figure #	Equation	Coefficient of Determination, R^2
1	All Sample Types	1A	[COD] = 2.4137[BOD_5] + 14.212	0.9283
2	Primary Effluent (Total)	1B	[COD] = 1.1419[BOD_5] + 202.73	0.3012
3	Primary Effluent (Dissolved)	1C	[COD] = 1.2973[BOD_5] + 55.554	0.3950
4	Final Effluent (Total)	1D	[COD] = 0.405[BOD_5] + 45.976	0.0184

Research Project: TOC Data



Equation #	Lab	Sample Type	Figure #	Equation	Coefficient of Determination, R^2
5	All	All	2A	[TOC] = 0.3633[BOD_5] + 18.153	0.6327
6	IIT	All	2A	[TOC] = 0.5100[BOD_5] + 17.0061	0.8698
7	SEP	All	2A	[TOC] = 0.2290[BOD_5] + 18.4434	0.6685
8	IIT	Primary Effluent (Total)	2A	[TOC] = 0.6201[BOD_5] + 1.1856	0.6950
9	SEP	Primary Effluent (Total)	2B	[TOC] = 0.0477[BOD_5] + 42.021	0.0074
10	IIT	Primary Effluent (Dissolved)	2C	[TOC] = 0.4531[BOD_5] + 22.591	0.4142
11	SEP	Primary Effluent (Dissolved)	2C	[TOC] = 0.2093[BOD_5] + 25.984	0.2480
12	IIT	Final Effluent (Total)	2D	[TOC] = 0.0465[BOD_5] + 22.75	0.0022
13	SEP	Final Effluent (Total)	2D	[TOC] = -0.1105[BOD_5] + 18.524	0.0260

Conclusions

- Further investigation to understand source of discrepancy between laboratories
- Lessons learned will contribute to objective (2): ‘Evaluating the performance and reliability of online TOC analyzers’
- Promising preliminary results.
- Results will aid in establishing procedures to be used for the modification of permits
  - What correlation are we seeking? (primary, final, dissolved, total or all?)
  - Why would we seek for that particular correlation?

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QUESTIONS?