

# A Sniff Test for Wastewater Analysis Data

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BPO Hamilton

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Lower Hutt



# Background: Classification of Water Quality Parameters

Parameter	Procedure	Type	Rating	Comment
Temperature	On-site / real-time	Absolute value (°C/K is a SI unit)	AAA	Important parameter, key driver of physical, chemical and biological processes, easy to measure, highly reliable, low maintenance sensors.
Dissolved Oxygen	On-site / real-time	Absolute value (mg/L) ≠ (%sat)	AAA	Important parameter, easy to measure, key indicator for ecosystem health and wastewater treatment plant operation, reliable, adequate sensors available, Temperature and atmospheric pressure correction are doable, easy to calibrate.
pH	On-site / real-time	Absolute value (-log of H <sup>+</sup> mole/L)	AAA	Important parameter, easy to measure, key indicator for wastewater treatment and ecosystem health, probes require maintenance.
ORP (Oxidation-Reduction Potential)	On-site / real-time	Summary value expressed in absolute mV	AAA-	Summary parameter influenced by several factors, easy to measure, probes require maintenance, should be a more important parameter for wastewater treatment. Probably the most underutilised and misinterpreted of all water quality parameters.
Conductivity Specific Cond. Salinity	On-site / real-time	Absolute value 25°C stand. value Derivative	AAA- AAA- AA	Summary parameter influenced by several factors Easy to measure, reliable low-maintenance sensor Some interpretation required, be careful around different salinity conversion scales.

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Temperature	On-site / real-time	Absolute value (°C/K is a SI unit)	AAA
Dissolved Oxygen	On-site / real-time	Absolute value (mg/L) ≠ (%sat)	AAA
pH	On-site / real-time	Absolute value (-log of H <sup>+</sup> mole/L)	AAA
ORP (Oxidation-Reduction Potential)	On-site / real-time	Summary value expressed in absolute mV	AAA-
Conductivity Specific Cond. Salinity	On-site / real-time	Absolute value 25°C stand. value Derivative	AAA- AAA- AA



# Background: Classification of Water Quality Parameters

Parameter	Procedure	Type	Rating	Comment
Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS)	Wet sample in lab	Absolute value (mg/L)	AAA AAA	Key parameter for wastewater treatment, representative sampling is important (solids tend to settle), sample is tolerant of some storage and transport, robust laboratory procedures. Ashing of sample for VSS needs to strike balance between full combustion and crystal water removal / calcination.
Total Solids (TS) and Volatile Solids (VS)	Wet sample in lab	Absolute value (mg/L)	AAA AAA	Key parameter for wastewater treatment, representative sampling is important (solids tend to settle), sample is tolerant of some storage and transport, robust laboratory procedures. Problems around volatile organics. Ashing of sample for VS needs to strike balance between full combustion and crystal water removal / calcination.
Chemical Oxygen Demand (COD)	Wet sample in lab	Proxy value expressed as oxygen equivalent (mg/L)	AAA	Summary value for all wastewater organics expressed in oxygen equivalent, representative sampling is important (solids tend to settle), sample often needs to be chilled or preserved to stop biological activity during storage and transport, robust laboratory procedures. COD can sometimes “overstate the issue” by counting in recalcitrant organics (lignin, etc.) which are inert in wastewater treatment.

# Background: Classification of Water Quality Parameters

Parameter	Procedure	Type	Rating	Comment
Nutrients: Phosphorus TP and DRP	Wet sample in lab	Absolute value (mg/L)	AAA	Ever-more important parameter for wastewater treatment, key driver for biology (eutrophication), representative sampling is important as sediment and sludge are P-rich, sample is tolerant of storage and transport, robust laboratory procedures.
Nutrients: Total nitrogen TN and TKN (Kjeldahl-N)	Wet sample in lab	Absolute value (mg/L)	AAA-	Key parameter for wastewater treatment, key driver for biology (eutrophication), representative sampling is important as sediment and sludge are N-rich, sample may require preservation for storage and transport, robust lab procedures.
Nutrients: Ammoniacal Nitrogen (NH <sub>4</sub> -N)	Wet sample in lab	Absolute value (mg/L)	AAA-	Key parameter for wastewater treatment, key driver for biology (eutrophication/toxicity), sample may require preservation for storage and transport, robust lab procedures.
	On-site selective ion electrode	Correlated mV signal	B-	Selective ion electrodes are maintenance intensive, unreliable, and subject to many interferences (poisoning).
Nutrients: Nitrate Nitrogen (NO <sub>3</sub> -N)	Wet sample in lab	Absolute value (mg/L)	AAA-	Key parameter for wastewater treatment, key driver for biology (eutrophication), sample may require chilling for storage and transport, robust lab procedures.
	On-site spectrophotometer	Light absorption at peak nm range as proxy	A-	Conflict between data resolution and range. Several interference factors (sediment, colour). Good in the right setting for long-term high-frequency data series, difficult for sporadic analysis of diverse waters.

# Background: Classification of Water Quality Parameters

Parameter	Procedure	Type	Rating	Comment
Chlorophyll a (Cla)	Wet sample in lab	Absolute value (mg/L)	AAA-	Key parameter for algal growth (eutrophication) in natural waters and wastewater. Challenge to obtain representative sample, robust lab procedures.
	On-site fluorescent probe	Fluorescence at 475nm as proxy	AA-	Relatively high interference at low Chlorophyll a concentrations, but 475nm is rather target specific.
Coloured / florescent dissolved organic matter	On-site / real-time CDOM / fDOM probe	Relative proxy value at instrument specific nm range	A-	Indicator for water discolouration. Important for some wastewater treatment plants and peat waters. Sensors work very reliable. Very difficult to specify absolute and comparable values, as no SI-unit compliant output is generated (relative %, or quinine sulphate equivalent). Site specific, (long) time-series has value.
Turbidity	On-site / real-time 90° light scattering nephelometers	Non-SI aligned formazine equivalent value (FNU / NTU)	?	Even ISO-7027-compliant nephelometers produce non-comparable numerical output. Turbidity meter output MUST be correlated to suspended sediment or water clarity. FNU/NTU units are meaningless. Turbidity meters from different manufacturers cannot be swapped / replaced. Individual, site specific correlation for each probe is required. For recreational waters the formazine scale is too coarse to really matter.
Water clarity	On-site / real-time Beam transmissometer (or black disc)	Absolute value in SI units (m <sup>-1</sup> )	AAA	Summary parameter combining water discoloration and fine sediment load (“turbidity”) into water clarity, measured in Absorption per meter. Important for recreational water use, water clarity measurement has good resolution at the important low end of the range.

# Background: Classification of Water Quality Parameters

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## RESEARCH ARTICLE

WILEY

### Weak numerical comparability of ISO-7027-compliant nephelometers. Ramifications for turbidity measurement applications

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#### Abstract

Nephelometric turbidity, a measure of light scattering by particles suspended in water, is commonly used for indicating water clarity or suspended particulate matter (SPM) concentration. Different turbidity sensors have long been known to respond differently to the same suspensions. Design standards have been introduced to improve comparability of turbidity sensors, notably the ISO-7027 standard adopted by a number of manufacturers. We compared six ISO-7027-compliant nephelometers in river silt, kaolinite (layer clay) and algae-laden pond water, with rigorous tank experiments over a wide (100-fold) concentration range. The responses of four different field-type (in situ) and two cuvette instruments, all calibrated to the same freshly made formazin standards, were very strongly linearly correlated, but ranged about twofold in magnitude. Apparently, even sensors meeting the same design standard (ISO-7027) cannot be relied on to output numerically similar formazin nephelometric unit (FNU) values. This weak numerical comparability highlights the futility of treating turbidity as an absolute quantity, for example in environmental standards or studies of fine SPM effects on aquatic life. Indeed, reporting of turbidity in informal units such as FNU is best avoided. Turbidity records should be converted, by site-specific calibrations, to quantities of ultimate interest such as SPM concentration or total phosphorus. For performance monitoring of field nephelometers, we advocate routine site-specific calibration, not to formazin, but to the light beam attenuation coefficient (beam-c; units:  $m^{-1}$ ). Beam-c is a proper (SI) physical quantity that can be precisely measured by beam transmissometry, as in our experiments, and is accurately convertible to visual clarity.

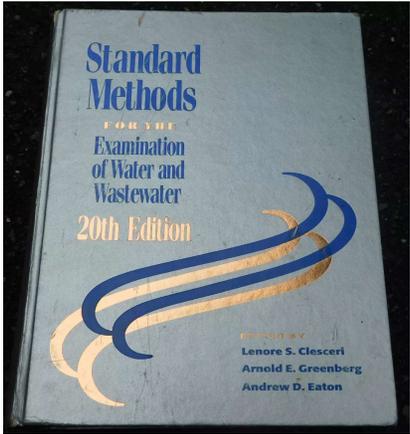
Parameter	Procedure	Type	Rating
Turbidity	On-site / real-time 90° light scattering nephelometers	Non-SI aligned formazine equivalent value (FNU / NTU)	?
Water clarity	On-site / real-time Beam transmissometer (or black disc)	Absolute value in SI units ( $m^{-1}$ )	AAA



Beam Transmissometers  
Source: Sea-Bird Scientific

# Background: Classification of Water Quality Parameters

Parameter	Procedure	Type	Rating	Comment
Oil and Grease	Wet sample in lab	Summary value of a wide range of equally soluble components	A-	Key parameter for protecting wastewater systems from blockage. For WW treatment and discharge not all that useful. Representative sampling can be difficult. Consistency of lab procedure and solvent is important. At low oil and grease levels a lot of interference is possible.
Total Petroleum Hydrocarbons	Wet sample in lab or gas chromatograph (GC)	Summary value of a wide range of equally soluble and/or volatile components	AA-	Key parameter for industrial wastewater and certain stormwaters, focused on petroleum inputs and associated toxicity issues. Representative sampling can be difficult. Problems around volatile hydrocarbon loss during storage, transport and analysis. GC use can overcome low-level issue, but comparability between different analysis methods difficult.



APHA Standard Methods (20th Edition, 1998) defines Oil and Grease, as analyzed with methods 5520 ff., as a parameter “defined by the method used for their determination”. Specifically, O&G “is defined as any material recovered as a substance soluble in the solvent” 80% n-hexane and 20% methyl-tert-butyl-ether.

# Background: Classification of Water Quality Parameters

Parameter	Procedure	Type	Rating	Comment
Bio-chemical Oxygen Demand (BOD <sub>5</sub> )	Wet sample in lab	Proxy value of bio-chemically available solids expressed as oxygen equivalent over arbitrary time frame (mg/L)	C-	Summary value for easily degradable wastewater organics expressed in oxygen equivalent. Sample needs to be chilled but cannot be preserved for storage and transport. Laboratory analysis introduces further uncertainty with biology (potency of spike). Time limitation often sees important contaminant load (e.g. true fats) underestimated. Overall the least reliable wastewater quality parameter.
E.Coli	Wet sample in lab	An indicator organism reported as most probable number	C-	E.Coli is not a water quality parameter. It is an indicator for faecal contamination, assumed to be closely correlated to the load / occurrence of true pathogens. E.Coli is a historical artefact. It should not even be used as a stand-alone proxy without further qualification (e.g. prescribed disinfection method). → Taumata Arowai draft national environmental wastewater discharge standards need to be substantially re-worked due to this oversight alone.

## Lesson 1: Adequate Parameter Selection

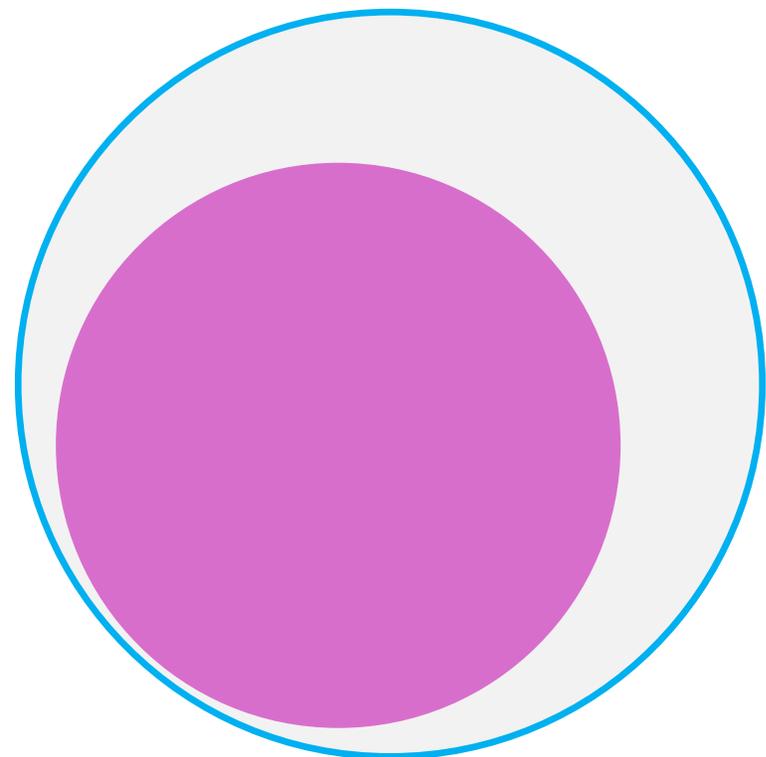
Water quality parameters differ. When designing a monitoring program, choose wisely:

- Select parameters recording absolute values.
- Choose robust technology, and maintain it.
- Check for interference and known “problem areas” upfront, for example:
  - pH readings in clean water need time to stabilize.
  - TS/VS and TSS/VSS test on high strength wastewater don't capture volatile organics - use COD test instead.
  - High suspended sediment concentrations interfere with all fluorescent and spectrophotometer probes.
  - Wastewater H<sub>2</sub>S interferes with most selective ion probes.
  - Testing for E.Coli in alkali waters tends to underestimate the issue.

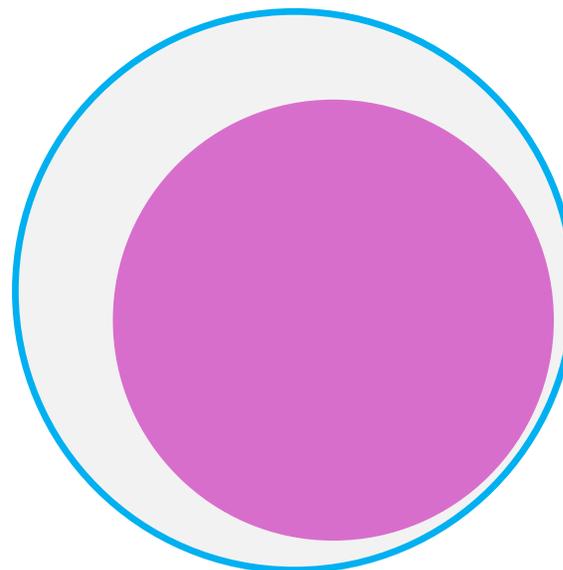
# Key Parameter Relationships

The solids:

$$TS = VS + \text{Ash}$$



$$TSS = VSS + \text{Ash}$$



$$TSS < TS$$

$$VSS < VS$$

Therefore

$$VSS < TS$$



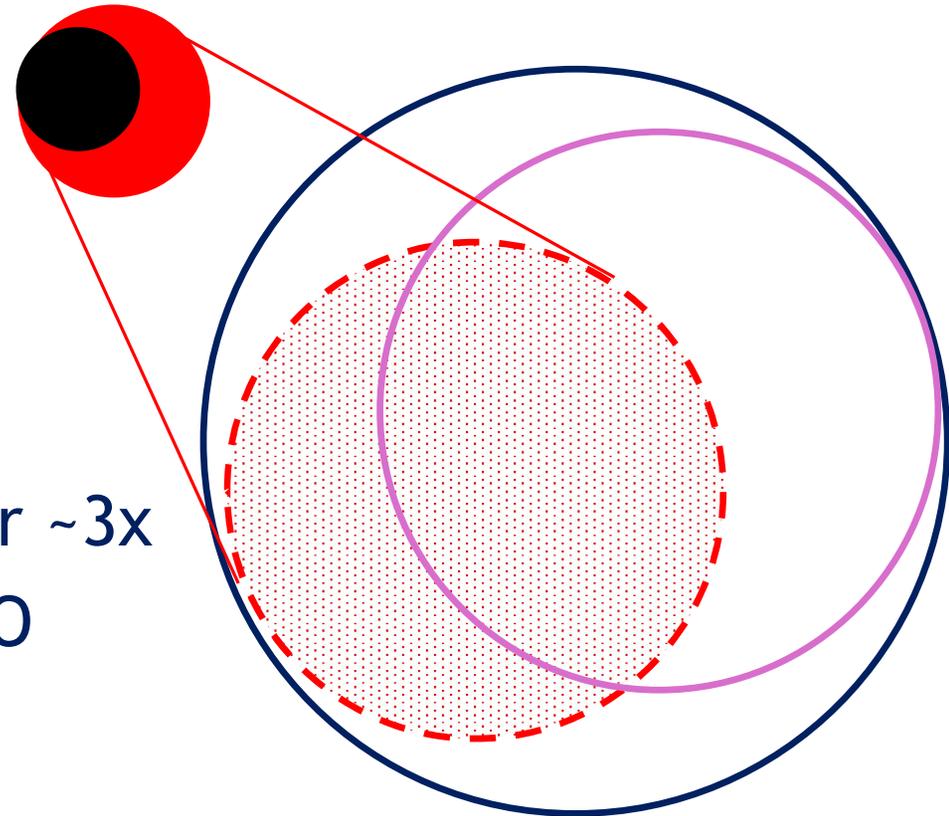
# Key Parameter Relationships

The solids:

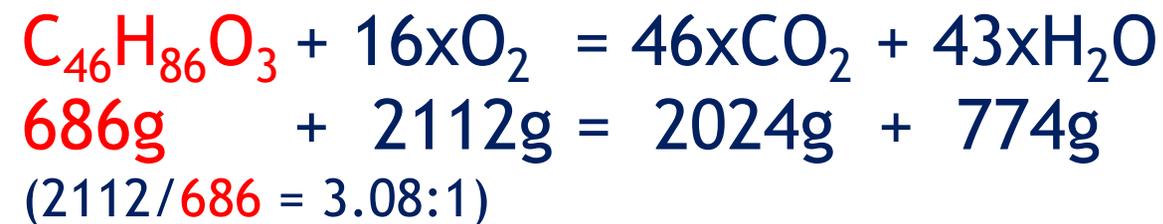


HC < O&G

BOD<sub>5</sub> < COD



Oil & Grease becomes COD at factor ~3x



# Key Parameter Relationships

## The nitrogen species

$$\text{Ammonia} + \text{org.N} = \text{TKN}$$

$$\text{TKN} + \text{oxidized N} = \text{TN}$$

Therefore:

$$\text{Ammonia} \leq \text{TKN}$$

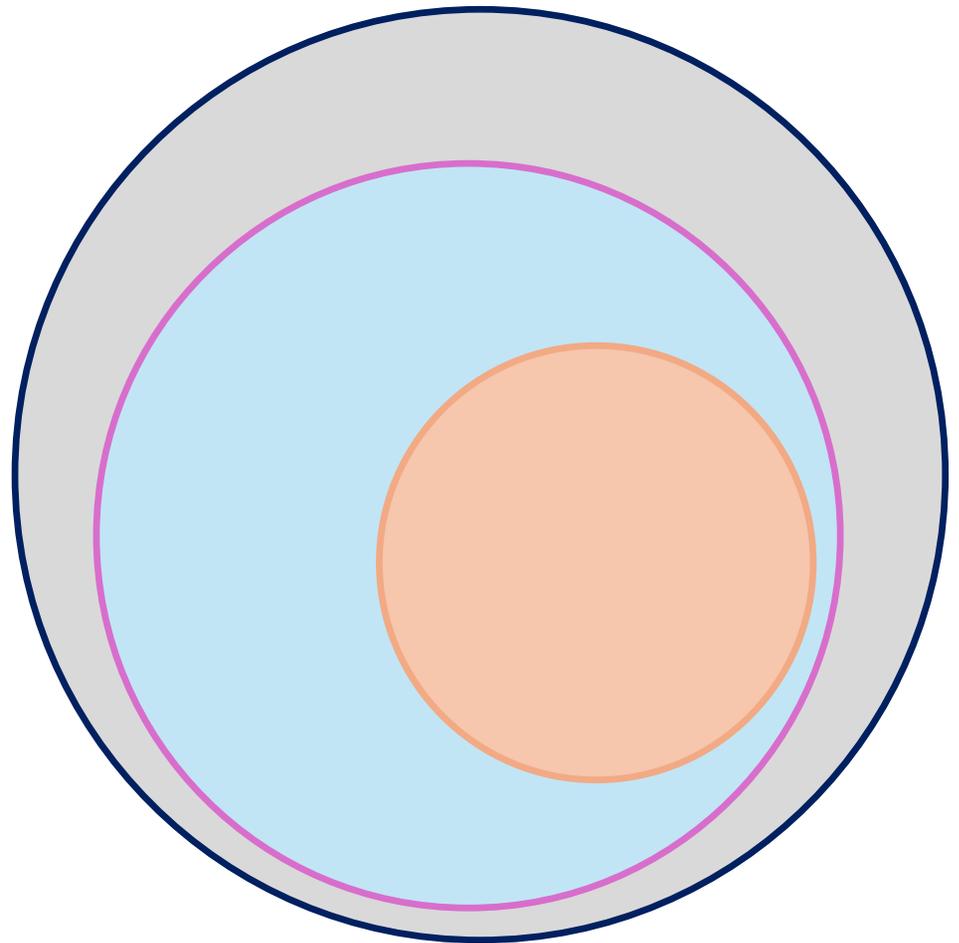
$$\text{org.N} \leq \text{TKN}$$

Furthermore:

$$\text{TKN} \leq \text{TN}$$

$$\text{Ammonia} \leq \text{TN}$$

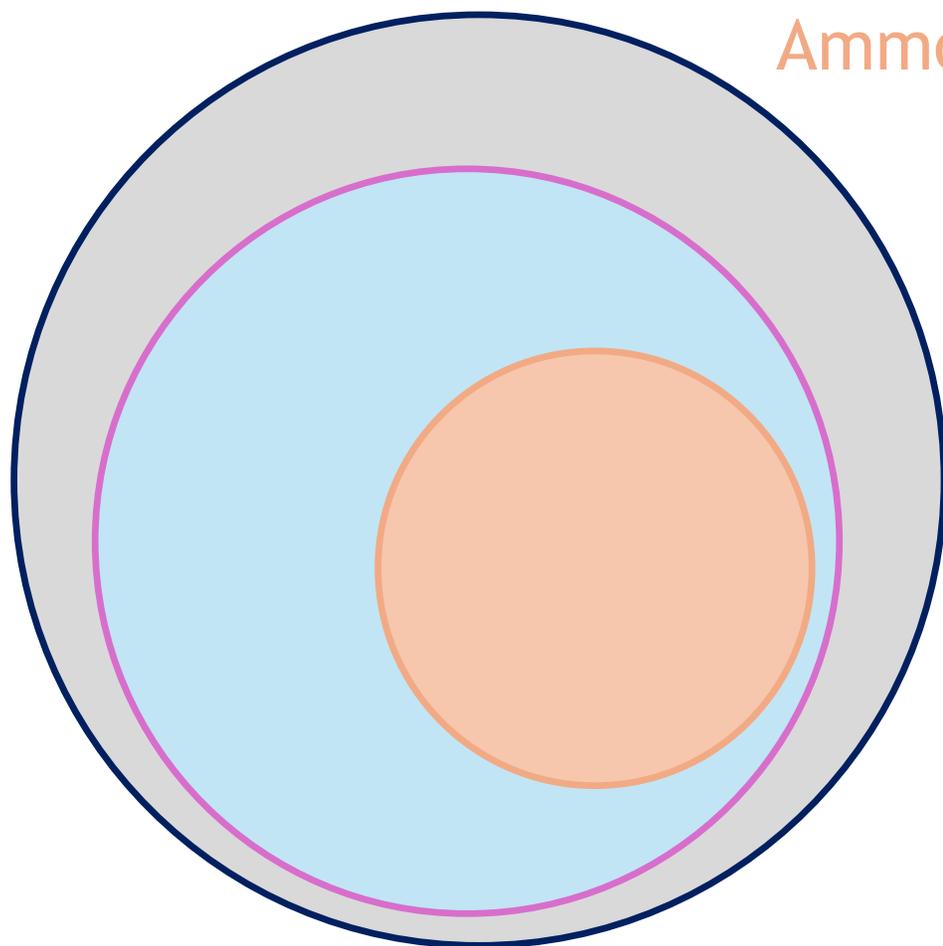
$$\text{org.N} \leq \text{TN}$$



# Key Parameter Relationships

## The nitrogen species

$$\text{Ammonia} + \text{oxidized N} = \text{Inorganic N}$$
$$\text{Inorganic N} + \text{org. N} = \text{TN}$$



Therefore:

$$\text{Ammonia} \leq \text{TN}$$

$$\text{oxidized N} \leq \text{TN}$$

$$\text{Inorganic N} \leq \text{TN}$$

## Lesson 2: Bigger tends to be better

Depending on the specific application, using the summary or overarching parameters often yields the most meaningful data, which is easiest to analyse, and tends to have less interference:

- Regarding receiving water eutrophication, and given sufficient time, nitrogen species tend to be interchangeable and the TN really counts (→ different for toxicity issues e.g. ammonia!).
- What level of granularity is required? If a WWTP struggles with aeration capacity, isn't it better to have more frequent COD data, rather than sporadic updates of the O&G, protein (organic N) and other fractions making up the COD?

## Lesson 3: Don't go looking for something that's not there!

Using the first principle relationships, it is easy to avoid some tests that are bound to not return anything:

### - ORP in wastewater example:

- ORP > +600mV → no living E.Coli (@ 1-5min time).
- ORP < ~+50mV → no free O<sub>2</sub> left (DO probe will show zero)
- ORP < ~-50mV → no nitrate left to find (e.g. in anoxic tank)

### Biochemical Reactions and Corresponding ORP Values

Biochemical Reaction	ORP, mV
Nitrification	+100 to +350
cBOD degradation with free molecular oxygen	+50 to +250
Biological phosphorus removal	+25 to +250
Denitrification	+50 to -50
Sulfide (H <sub>2</sub> S) formation	-50 to -250
Biological phosphorus release	-100 to -250
Acid formation (fermentation)	-100 to -225
Methane production	-175 to -400

## Lesson 3: Don't go looking for something that's not there!

Using the first principle relationships, it is easy to avoid some tests that are bound to not return anything:

- If O&G is zero or low, then Petroleum Hydrocarbons also have to be zero or low.
- If COD is zero or low, then BOD<sub>5</sub> and O&G also have to be zero or low.
- If CDOM/fDOM or fine sediment concentration (“Turbidity reading”) is moderate to high, water clarity measurements will be in the Abs/mm range and therefore meaningless. The reverse is true as well (see photo).



## Lesson 4: Check analysis method fine print!

Every analysis method will be associated with a specific detection limit, a maximum range as well as sensitivity/granularity. Before sampling and analysis, check that these aspects fit with your water sample and/or RC limits:

- For several parameters high- and low level test procedures are available.
- Some tests, like E.Coli and BOD<sub>5</sub>, often require sample dilution and a best guess about dilution rate → danger!
- Particularly regarding resource consent limits, ensure detection limit and discharge limit are not too close.

## Field example: Proving a lab error via mass balance

A stormwater discharge consent has limits of:

- TSS <30mg/L
- BOD<sub>5</sub> <10mg/L
- O&G <5mg/L
- Thankfully, COD was also analysed (for reasons of consistency).

Sample Type: Aqueous		A	B	C
Total Suspended Solids	g/m <sup>3</sup>	4	31	< 3
Dissolved C-Biochemical Oxygen Demand (CBOD <sub>5</sub> )	g O <sub>2</sub> /m <sup>3</sup>	1.8	2.0	3.4
Total Biochemical Oxygen Demand (TBOD <sub>5</sub> )	g O <sub>2</sub> /m <sup>3</sup>	3.6	13	2.1
Chemical Oxygen Demand (COD)	g O <sub>2</sub> /m <sup>3</sup>	16	52	8
Oil and Grease	g/m <sup>3</sup>	7	83	26

- *None of the O&G to COD ratios make sense.*
- *COD needs to be at least 3x O&G.*
- *(If O&G would be correct higher BOD<sub>5</sub> readings would also be expected, but ....)*

# Field example: Set up to fail via detection limit.

A stormwater discharge consent has limits of:

- TSS <30mg/L
- BOD<sub>5</sub> <10mg/L
- O&G <5mg/L
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Sample Type: Aqueous			
Test	Method Description	Default Detection Limit	Sample No
Total Suspended Solids	Filtration using Whatman 934 AH, Advantec GC-50 or equivalent filters (nominal pore size 1.2 - 1.5µm), gravimetric determination. APHA 2540 D (modified) : Online Edition.	3 g/m <sup>3</sup>	1-4
Dissolved C-Biochemical Oxygen Demand (CBOD <sub>5</sub> )	Filtered sample (1.2µm glass fibre filter), Incubation 5 days, CBOD <sub>5</sub> , DO meter, nitrification inhibitor, seeded. In-house.	1.0 g O <sub>2</sub> /m <sup>3</sup>	2-4
Total Biochemical Oxygen Demand (TBOD <sub>5</sub> )	Incubation 5 days, DO meter, no nitrification inhibitor added, unseeded. In-house.	0.4 g O <sub>2</sub> /m <sup>3</sup>	2-4
Chemical Oxygen Demand (COD), trace level	Dichromate/sulphuric acid digestion in Hach tubes, colorimetry. Trace Level method. APHA 5220 D : Online Edition.	6 g O <sub>2</sub> /m <sup>3</sup>	2-4
Chemical Oxygen Demand (COD), screen level	Dichromate/sulphuric acid digestion, colorimetry. Screen Level method. APHA 5220 D : Online Edition.	25 g O <sub>2</sub> /m <sup>3</sup>	1
Oil and Grease	Sample filtration through filter aid, Soxhlet extraction, gravimetric determination of extracted Oil & Grease. APHA 5520 D (modified) : Online Edition.	4 g/m <sup>3</sup>	1-4

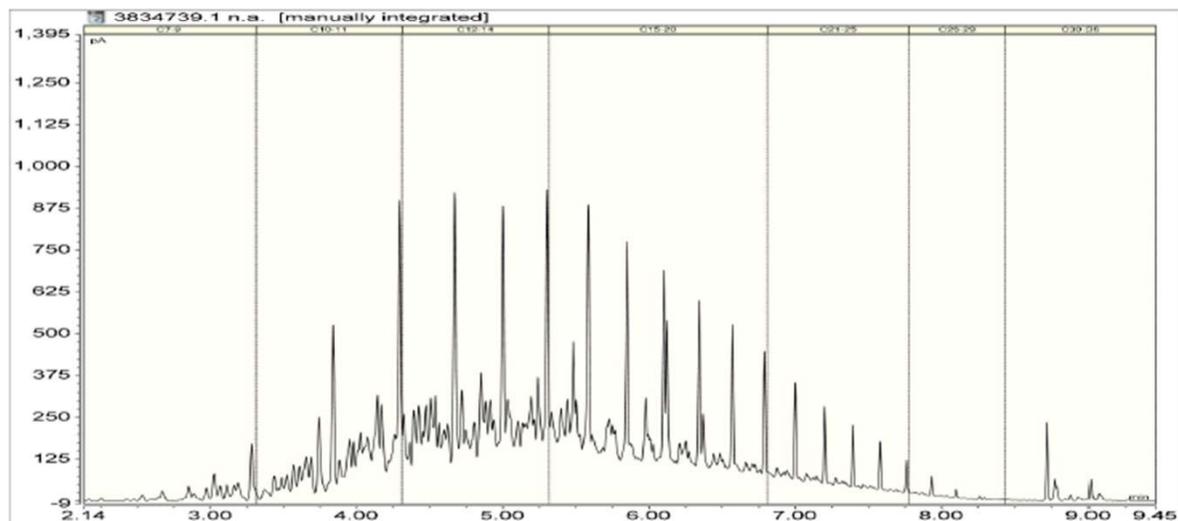
- An O&G detection limit of 4 mg/L to meet RC limit of 5 mg/L.
- Could O&G test follow a >15mg/L COD?

# Field example: Proving a lab error via mass balance

O&G “is defined as any material recovered as a substance soluble in the solvent”  
80% n-hexane and 20% methyl-tert-butyl-ether).

Sample Type: Aqueous			
Sample Name:			
Lab Number:			
Individual Tests			
Total Kjeldahl Nitrogen (TKN)	g/m <sup>3</sup>	1,070	
Oil and Grease	g/m <sup>3</sup>	22,000	
Total Petroleum Hydrocarbons in Water			
C7 - C9	g/m <sup>3</sup>	2,600	
C10 - C14	g/m <sup>3</sup>	55,000	
C15 - C36	g/m <sup>3</sup>	56,000	
Total hydrocarbons (C7 - C36)	g/m <sup>3</sup>	114,000	

Client Chromatogram for TPH by FID



A Sniff Test for Wastewater Analysis Data

# Q&A

Let's talk about your analysis issue

**Stephan Heubeck**

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