→ **Tim Mulliner**
Technical Director – Environment

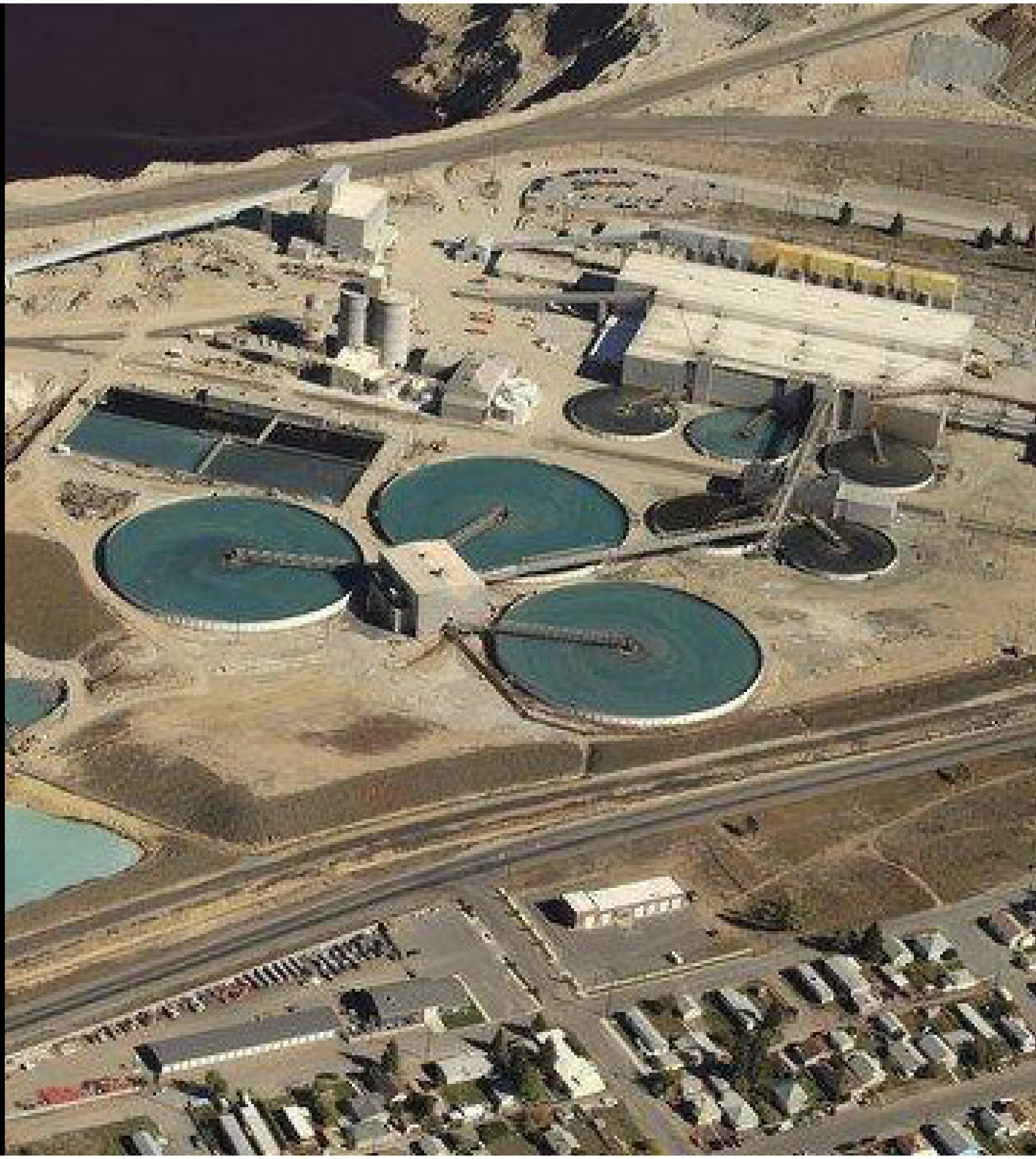
→ **Jack Thomas**
Technical Lead – Environmental Engineer

Nitrogen compounds and mine impacted surface waters

↳ Chemistry, regulation and treatment

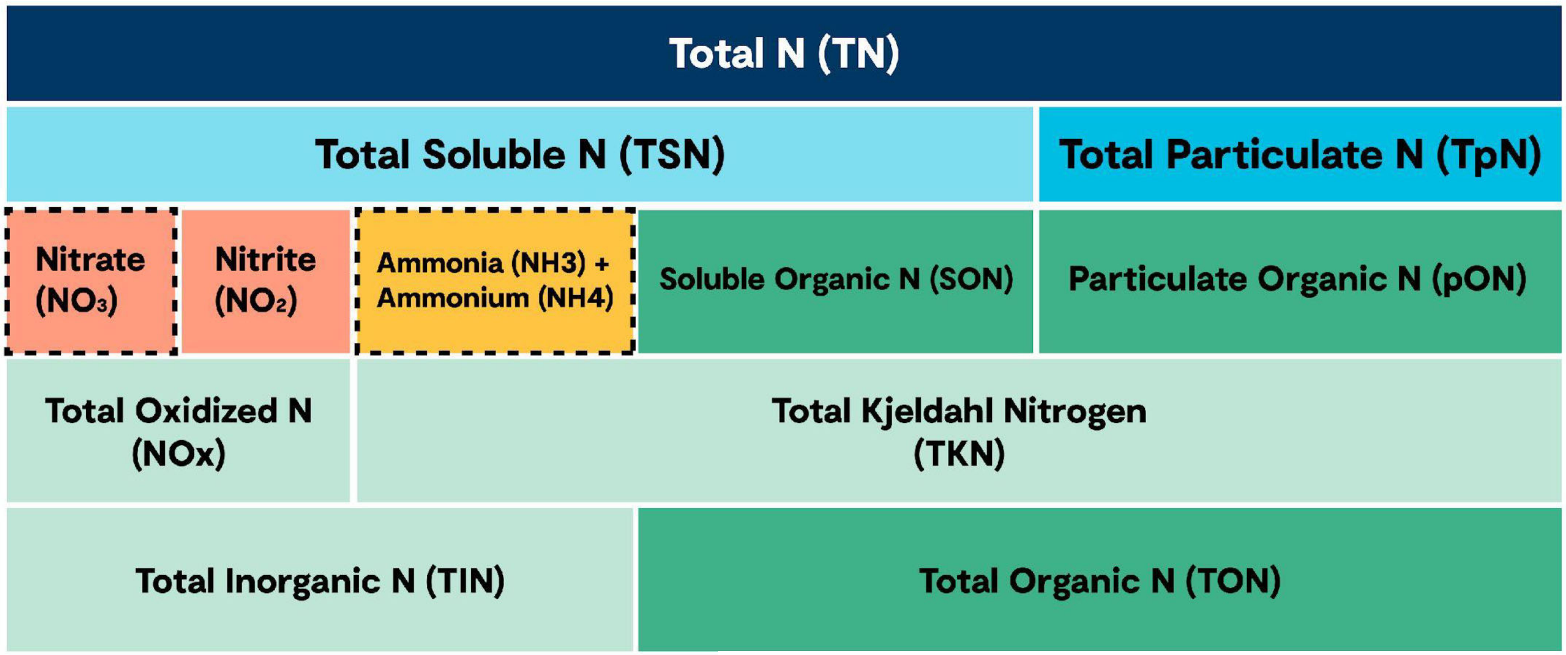
Outline

→ **Nitrogen Compounds**
Regulation
Treatment



→ Nitrogen compounds / cycle

Nitrogen compounds

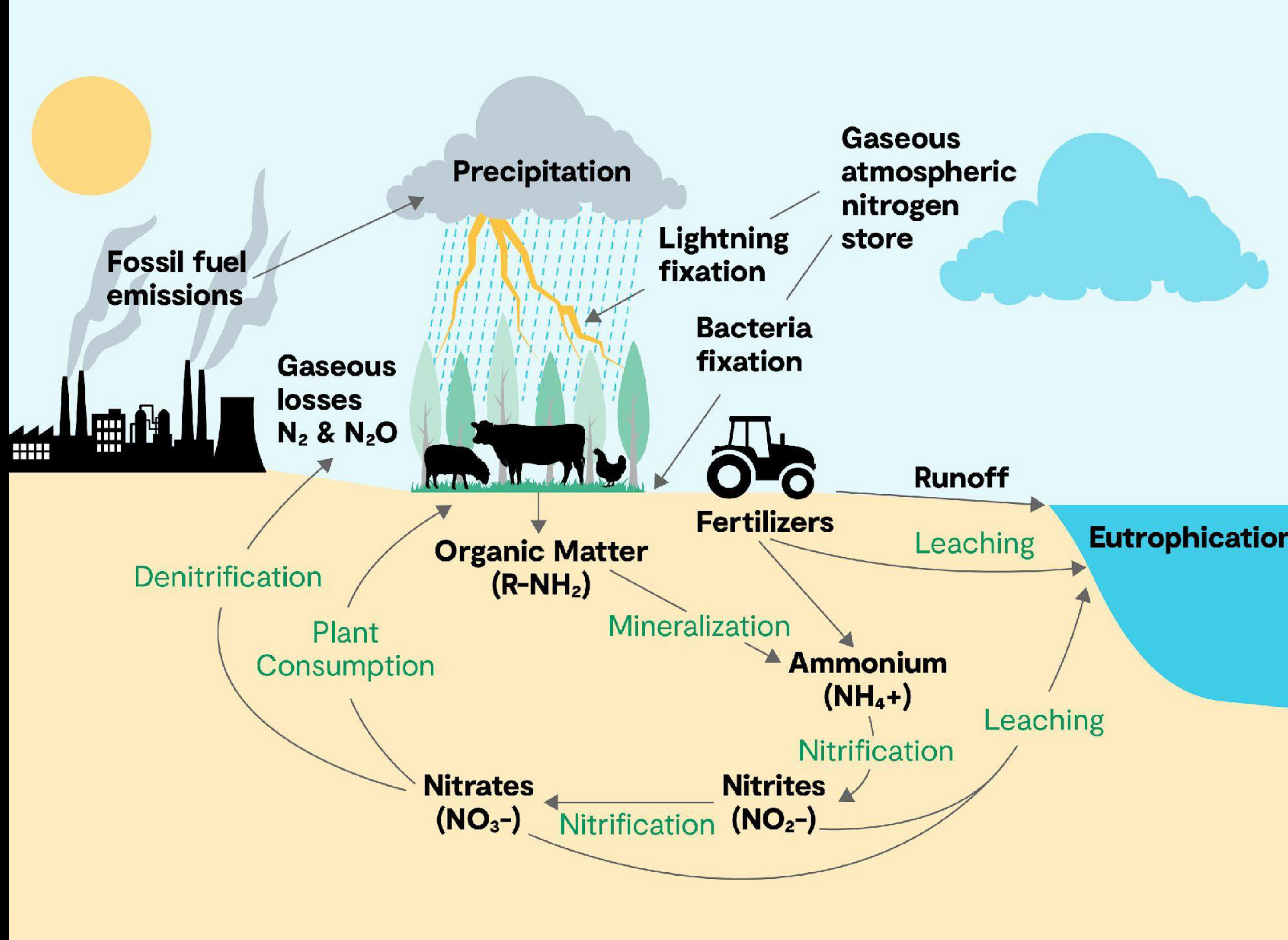


https://www.lawa.org.nz/learn/factsheets/nitrogen/

Sources from Mining Operations – Natural (e.g. Otago Schist), Blasting residues

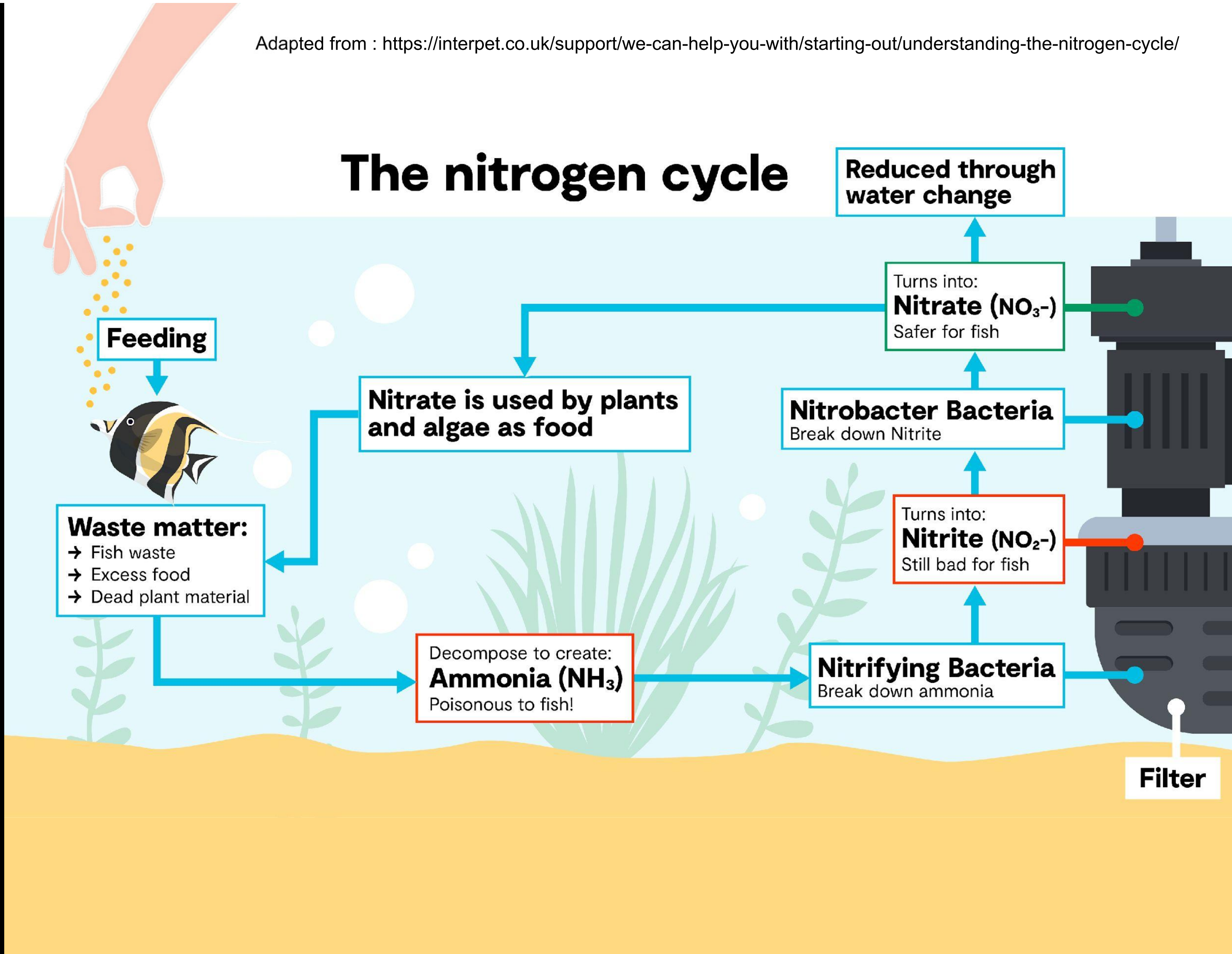
Nitrogen in the environment

Adapted from : http://www.physicalgeography.net/fundamentals/9s.html



Nitrogen in the environment

Adapted from : https://interpet.co.uk/support/we-can-help-you-with/starting-out/understanding-the-nitrogen-cycle/



→ Regulation

Regulation

National Policy Statement for Freshwater Management 2020

August 2020

Table 5 - Ammonia (toxicity)

Value (and component)	Ecosystem health (Water quality)	
Freshwater body type	Lakes and Rivers	
Attribute unit	mg NH_4-N/L (milligrams ammoniacal-nitrogen per litre)	
Attribute band and description	**Numeric attribute state**	
	Annual median	**Annual maximum**
A 99% species protection level: No observed effect on any species tested.	≤0.03	≤0.05
B 95% species protection level: Starts impacting occasionally on the 5% most sensitive species.	>0.03 and ≤0.24	>0.05 and ≤0.40
National bottom line	**0.24**	**0.40**
C 80% species protection level: Starts impacting regularly on the 20% most sensitive species (reduced survival of most sensitive species).	>0.03 and ≤0.24	>0.05 and ≤0.40
D Starts approaching acute impact level (that is, risk of death) for sensitive species.	>1.30	>2.20
Numeric attribute state is based on pH 8 and temperature of 20°C. Compliance with the numeric attribute states should be undertaken after pH adjustment.		

Table 6 - Nitrate (toxicity)

Value (and component)	Ecosystem health (Water quality)	
Freshwater body type	Rivers	
Attribute unit	mg NH_3-N/L (milligrams nitrate-nitrogen per litre)	
Attribute band and description	**Numeric attribute state**	
	Annual median	**Annual 95th percentile**
A High conservation value system. Unlikely to be effects even on sensitive species.	≤1.0	≤1.5
B Some growth effect on up to 5% of species.	>1.0 and ≤2.4	>1.5 and ≤3.5
National bottom line	**2.4**	**3.5**
C Growth effects on up to 20% of species (mainly sensitive species such as fish). No acute effects.	>2.4 and ≤6.9	>3.5 and $9.8
D Impacts on growth of multiple species, and starts approaching acute impact level (that is, risk of death) for sensitive species at higher concentrations (>20 mg/L).	>1.30	>2.20
This attribute measures the toxic effects of nitrate, not the trophic state. Where other attributes measure trophic state, for example periphyton, freshwater objectives, limits and/or methods for those attributes may be more stringent.		

Table 3 - Total nitrogen (trophic state)

Value (and component)	Ecosystem health (Water quality)	
Freshwater body type	Lakes	
Attribute unit	mg/m_3 (milligrams per cubic metre)	
Attribute band and description	**Numeric attribute state**	
	Annual median	**Annual 95th percentile**
	Seasonally stratified and brackish	Polymictic
A Lake ecological communities are healthy an resilient, similar to natural reference conditions.	≤160	≤300
B Lake ecological communities are slightly impacted by additional algal and/or plant growth arising from nutrient levels that are elevated above natural reference conditions.	>160 and ≤350	>300 and ≤500
C Lake ecological communities are moderately impacted by additional algal and plant growth arising from nutrient levels that are elevated well above natural reference conditions.	>350 and ≤750	>500 and ≤800
National bottom line	**750**	**800**
D Lake ecological communities have undergone or are at high risk of a regime shift to a persistent, degraded state (without native macrophyte/seagrass cover), due to impacts of elevated nutrients leading to excessive algal and/or plant growth, as well as from losing oxygen in bottom waters of deep lakes.	>750	>800
For lakes and lagoons that are intermittently open to the sea, monitoring data should be analysed separately for closed periods and open periods.		

Nitrate N – Check your lab report!

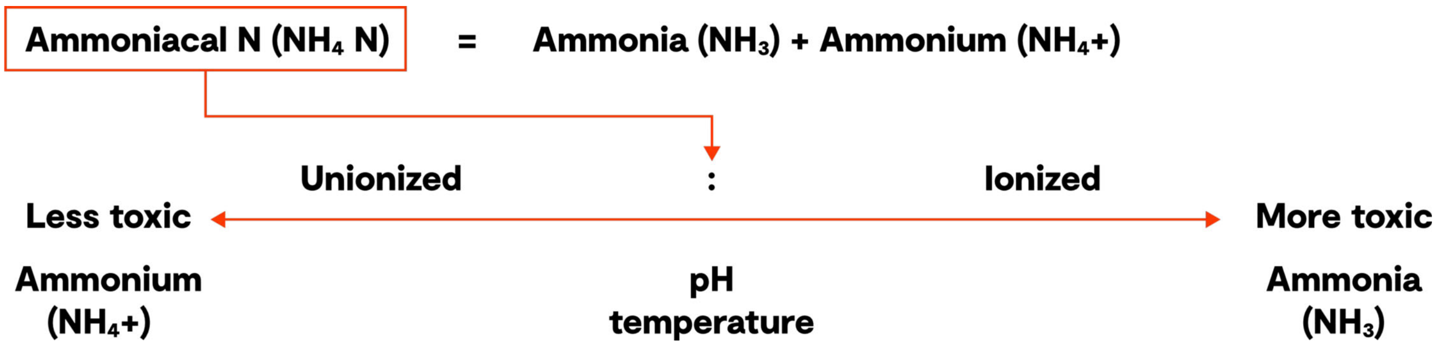
Nitrate (NO_3) ≠ Nitrate -N (NO_3-N)

Nitrate is one part nitrogen plus three parts oxygen so nitrogen only makes up about 22.6% of the nitrate ion nitrogen **only makes up about 22.6 percent on the nitrate ion**

Nitrate (NO_3) ≠ Nitrate Nitrogen * 4.43

Nitrate * 0.26 ≠ Nitrate Nitrogen

Ammonia is the molecule (free ammonia, generally a gas),
Ammonium is the ionized form (ie. forms bonds e.g. with water)



MFE. A Guide to Attributes In Appendix 2 of the National Policy Statement for Freshwater Management 2014 (as amended 2017)

Table 10: Conversion ratios for pH adjustment of ammonia concentrations

Sample pH	Ratio	Sample pH	Ratio	Sample pH	Ratio
6	2.86	7	2.42	8.1	0.87
6.1	2.84	7.1	2.32	8.2	0.73
6.2	2.82	7.2	2.21	8.3	0.62
6.3	2.80	7.3	2.09	8.4	0.53
6.4	2.77	7.4	1.94	8.5	0.44
6.5	2.73	7.5	1.79	8.6	0.38
6.6	2.70	7.6	1.63	8.7	0.32
6.7	2.64	7.7	1.47	8.8	0.27
6.8	2.59	7.8	1.31	8.9	0.23
6.9	2.51	7.9	1.14	9	0.20
		8	1.00	>9	0.20

Source: Adapted from ANZECC (2000) and Hickey (2014).

$$Conc_{pH\ 8} = \frac{Conc_{pH\ sample}}{Ratio} \qquad \text{Equation (1)}$$

Where $Conc_{pH\ sample}$ is the concentration of the sample and $Ratio$ is read from table 10 for the given sample pH.

For example, if a sample was observed with 1.12 mg NH_4-N/L at pH 7.5, the adjusted concentration to use in calculating sample statistics would be 0.63 mg NH_4-N/L at pH 8. This is derived as follows:

Using equation (1) and table 10:

$$Conc_{pH8} = 0.63 = \frac{1.12}{1.79}$$

Where the numerator (1.12) is the observed sample concentration and the denominator (1.79) is the $Ratio$ from table 10 at pH of 7.5.

That is, although there is still 1.12 mg/L of NH_4-N present in the sample, the adjustment process has identified that the toxicity of this sample at pH 7.5 is equivalent to the toxicity associated with a NH_4-N concentration of 0.63 mg/L at pH 8. It's the equivalent toxicity that has been adjusted, and not the amount of NH_4-N present in the sample (which remains unchanged).

→ Treatment

Treatment of Ammoniacal N and Nitrate in Water

Treatment techniques will depend on many variables including:

- ➔ Do both ammoniacal N and nitrate need to be treated?
- ➔ What are influent concentrations and what targets need to be achieved?
- ➔ Presence of co-contaminants? (ideally removed prior)
- ➔ Is treatment continuous or sporadic?

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Treatment – Biological or Physico-chemical

Biological treatment – changes form of N, potentially to N_2 gas (if nitrification > denitrification carried out)

- Nitrification: converts ammonia to nitrate via nitrite
- Denitrification: converts nitrate to nitrogen gas

Physico-chemical treatment techniques vary as to their mechanism:

- Concentration: e.g. RO, IX concentrate the contaminant into a waste stream
- Destruction: e.g. break-point chlorination
- Phase change: e.g. air stripping of ammonia


GHD Library Image


GHD Library Image

Treatment – Biological

Nitrification (converting ammonia to nitrate)

- Requires oxygen, suitable pH and temperature
- Provision of a suitable growth substrate enhances process
  - Aeration pond
  - Activated sludge

Larger footprint

- Sequential Batch Reactor (SBR) – can also be configured for denitrification
- Moving Bed Biofilm Reactor (MBBR)
- Membrane Bioreactor (MBR)

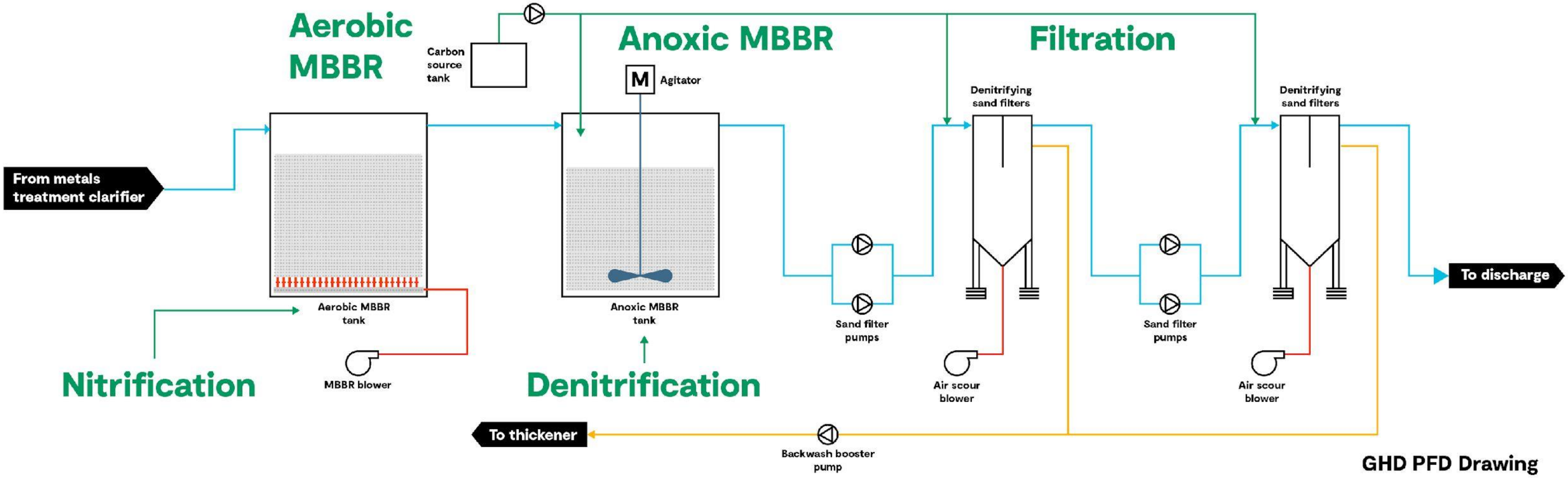
Compact Plant

- **Deitrification (converting nitrate to N_2 gas)**
- Requires anoxic conditions, carbon source, suitable pH and temperature

Treatment – Biological

Moving Bed Biofilm Reactor (MBBR)

- Nitrification (NH_3/NH_4^+ to NO_3) by aerating tank half filled with plastic media
- Denitrification (NO_3 to N_2 gas) by dosing carbon source and mechanically mixing in anoxic conditions



Treatment – Biological

Downsides

- Susceptible to shock loading
- Need regular flow
  (no major hiatus) to sustain microbial population
- pH may need adjusting if influent is <6.5 or >8.5
- Temperature – efficiency drops significantly <10°C with (usually) poor efficiency <5°C
- Trained operators needed

Treatment – Physico-chemical

→ **Ammoniacal nitrogen treatment methods include:**

- Air stripping
- Break point chlorination
- Natural media ion exchange (for NH_4^+) – zeolite
- Ion exchange resin (for NH_4^+) – Nitrate can also be treated

} Up to 99% efficiency

→ **Nitrate treatment– more expensive / complicated**

- Nitrate-selective ion-exchange resin → 80-99% efficiency
- Reverse osmosis → 50-95% efficiency
- Electrodialysis → 30-80% efficiency

→ **Best carried out after solids (and other contaminants) removal**

Passive zeolite system

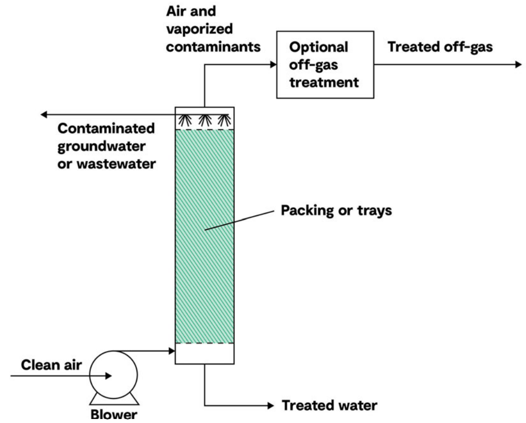
Ion exchange vessels

Air stripping by aeration

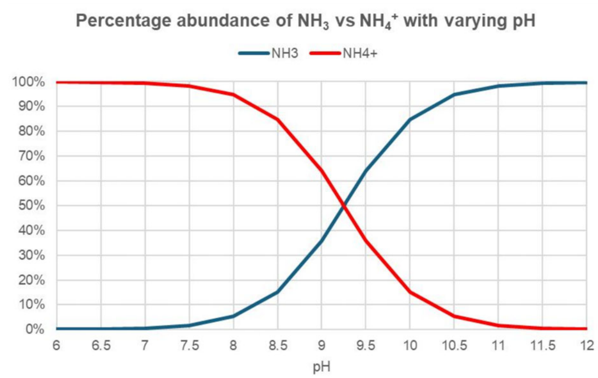
Treatment – Physico-chemical

Air stripping (ammonia only):

- pH needs to be above 10.5 to be effective (over 11 for optimum efficiency)
- Ammonia has relatively low vapour pressure – lots of air contact needed to strip
- Long residence in aeration pond or;
- >200:1 air : water ratio in a packed air stripping tower
- Efficiency is also temperature dependent
- Acid dosing often needed prior to discharge



From: https://frtr.gov/matrix/Air-Stripping-Ex-Situ/



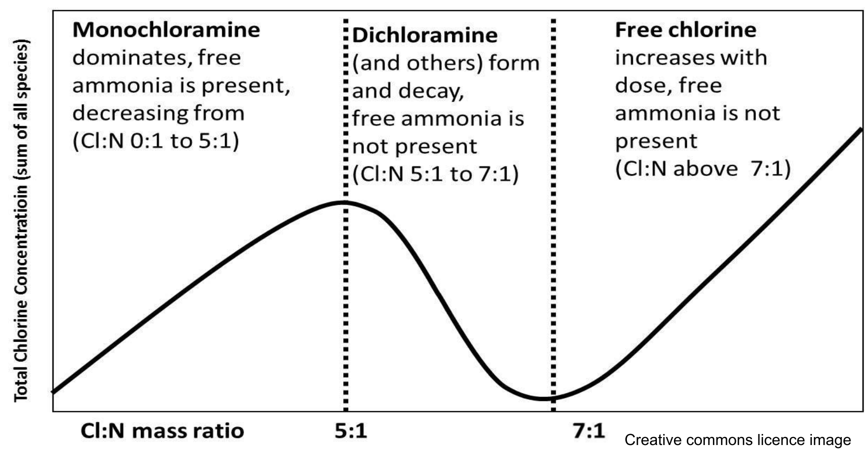
Air stripping packed tower

Air stripping pond

Treatment – Physico-chemical

Break-point chlorination (ammoniacal N only):

- Chlorine is added (usually as hypochlorite) until free chlorine is detected
- Converts ammoniacal nitrogen to N_2 gas
- Late-stage treatment process to prevent unnecessary chlorine usage (Fe, Mn, TOC will consume)
- Mixing is carried out in a reaction tank
- Post-reaction removal of excess chlorine is usually needed – GAC sorption



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GAC vessels for excess chlorine removal

Treatment – Physico-chemical

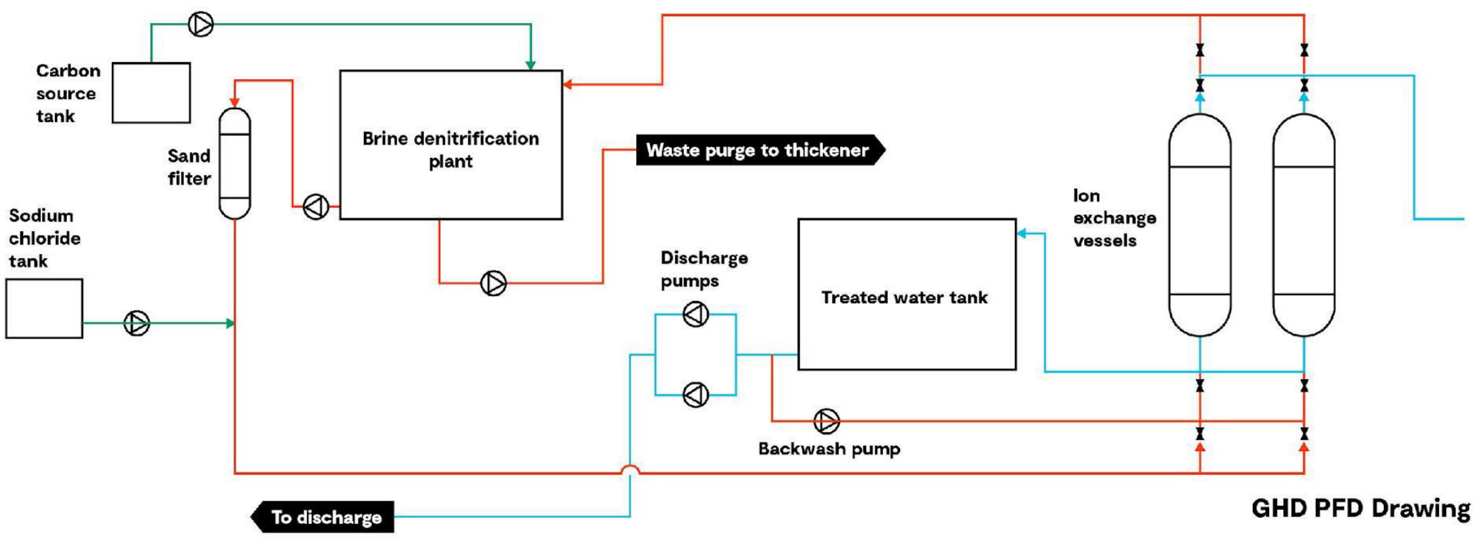
Ion-exchange processes (ammonium and nitrate):

Natural media such as zeolite is inexpensive for NH_4^+ removal but becomes spent rapidly – only cost effective for lower concentrations in low TDS waters

Zeolite not suitable for higher influent NH_4^+ concentrations, best used as a polishing media

Ion exchange resins are effective for a greater range of influent concentrations, but require regeneration

NaCl solution often used to regenerate resins – waste solution requires treatment / disposal



GHD PFD Drawing

→ Summary

Summary

- Nitrate versus Nitrate N
- Ammoniacal N – need to adjust to ascertain compliance equivalence
- Different requirements based on different forms
- Nitrate N treatment is costly

The end

tim.mulliner@ghd.com

jack.thomas@ghd.com