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Executive Summary

The Mount Lyell Remediation Research and Development Program, a long term monitoring program, was established in the 1995. This EPA report has reviewed the nutrient data from 2013 to 2016, and includes those sites where there is historic data for the period from 1995 to 1997.

The review has identified some total and dissolved nutrient species concentrations have increased in Macquarie Harbour when considering historic and current water quality data. The levels observed in the central harbour and WHA infer additional nutrient inputs other than those entering from the Gordon River or marine waters are occurring. Some key points are as follows:

- **Total Nitrogen** time series plots reflect elevated nitrogen in bottom waters of the World Heritage Area and the Northern Harbour. Site WHA4 had the greatest range in bottom waters of the WHA with a minimum TN of 240 µg/L to a maximum of 400 µg/L. In the Northern Harbour, Site MH12 had the greatest range of TN with a minimum of 210µg/L to a maximum value of 420 µg/L.
- The greatest range of **Total Kjeldahl Nitrogen (TKN)** occurred in the bottom waters of the WHA and North Harbour sites. Nitrogen in the surface waters of all areas of the harbour is dominated by organic N (TKN) with a considerable contribution being made by flows from the Gordon River.
- A relatively small fraction of TN is composed of dissolved inorganic nitrogen (10-20%) in surface waters where as for bottom waters in the WHA and North Harbour sites a much greater proportion of NOx (30-40%) makes up the nitrogen species.
- NOx in the surface waters ranged from a minimum of 2 µg/L in the North Harbour transect to a maximum of 69 µg/L at the Gordon River site. In bottom waters the range was greater with a minimum value of 7 µg/L recorded in the Kelly Channel and maximum values of 140 µg/L being observed in both the WHA and North Harbour transects.
- Median values for NOx in surface waters were highest at the North Harbour sites (43 µg/L) and WHA (38 µg/L) and more than twice the median values observed over a period between 1995 and 1997 for similar sites of 18 µg/L and 11 µg/L respectively. For bottom waters median NOx values were highest in the WHA and Northern Harbour areas (120 µg/L and 100 µg/L respectively). These levels were considerably higher than historic median values for similar sites of 58.5 µg/L (MH27,32,34) and 50 µg/L (MH11,12,13,14) respectively for the 1995 to 1997 period.
- NOx collected from waters in the upper reaches of the Gordon River including a site above the confluence of the Franklin at the beginning of the sampling period (quarterly from Nov 2012 until Nov 2013) were similar in scale to those at the Gordon River and Kelly Channel sites and ranged in concentration from 10µg/L to 42µg/L. Historic harbour values (1995-1997) and current riverine and Kelly Channel derived NOx values are similar in magnitude.
- NOx levels in bottom waters at the Gordon River site are related to salt water intrusion from the harbour proper. The highest NOx value (110µg/L) occurring with a salinity of 23.4 PSU; the linear regression of Salinity/NOx for this site has an \( R^2 \) value of 0.67.
- In the harbour, WHA and central harbour sites, the median ammonia and ammonium levels in bottom waters were 5 µg/L and 6.6 µg/L respectively, approximately half of those in the surface waters (12 µg/L and 13 µg/L respectively).
- Both TP and DRP concentrations are highest in the harbour (WHA and North Harbour sites) and lower in the riverine waters of the Gordon and marine waters.
- Comparing historic values to recent values there has been a harbour wide increase in DRP with the most significant elevation in DRP occurring in the bottom waters in both the Northern Harbour and WHA sites.
Introduction

Macquarie Harbour has been monitored under various programs but one of the long term programs is the Mount Lyell Remediation Research and Development Program (MLRRDP) which was established in the 1995. Through this program many years of data have been collected within the harbour and for shorter periods within the Gordon and King Rivers. The map below illustrates a subset of the sites which are still being monitored and some additional sites.

In response to extended periods of depressed dissolved oxygen levels in Macquarie Harbour (MH) the routine quarterly monitoring was expanded to include a number of sites in the World Heritage Area (WHA) including the Gordon River and a site in Kelly Channel near the mouth of the harbour. The parameters monitored at these sites included the regular suite of metals as well as total and dissolved nutrients, total suspended solids and organic carbon. Nutrients were also added to the usual parameters collected at a number of long term monitoring sites (MH11, MH12 and MH14) in the Northern Harbour to give a measure of water quality throughout the greater harbour.

The sites added to the monitoring program in the WHA detailed in the map above are denoted: WHA3 (7km up river from the mouth of the Gordon), and WHA4, WHA5, and WHA6 in part of the World Heritage Area on of Macquarie Harbour. Site MH18 located in the Kelly Channel was reactivated but still considered a long term site. Sites MH11, MH12 and MH14 are also long term sites that had nutrients added to the parameters collected in 2013.
Data considerations

Samples are taken from these sites on a quarterly basis at three depths: Surface (<0.5m), Middle (at the 20psu halocline) and Bottom (1m above the harbour floor).

ANOVA analysis facilitated the aggregation of data for WHA4, WHA5 and WHA6 for all nutrient species except for NOx (Nitrite and Nitrate) of the bottom waters, which were deemed too dissimilar from the other sites to be included as an aggregate.

After ANOVA analysis of MH11, MH12 and MH14 nutrient data for these sites were aggregated for all depths (i.e., S, M, B).

Box and whisker plots presented below follow a transect from South East to North West along the Harbour. With WHA3 being within the Gordon River. Aggregated sites WHA4, WHA5 and WHA6 being the section of the Harbour falling within the WHA. Aggregated sites MH11, MH12 and MH14 being representative of water in the Northern Harbour and MH18 being at the mouth of the harbour.

In the box and whisker graphs the lower and upper levels of the boxes represent the 20th and 80th percentiles, the dots represent the median, and the whiskers extend to the minimum and maximum values.

Nutrient data review

Nutrient data from 2013 has been reviewed and those sites where historic data exists, i.e. 1995-1997, it has also been included.

Total Nitrogen (TN)

Total Nitrogen (TN) is the sum of inorganic (nitrate-nitrogen (NO$_3$-N), nitrite-nitrogen (NO$_2$-N), total ammonia-nitrogen (NH$_3$/NH$_4$-N) and organic nitrogen. This measure is used because nitrogen change between these nitrogen species within the water body.

For the 2013-2016 period median Total Nitrogen (TN) values ranged from 220µg/L in surface waters of the majority of the harbour (not including the Gordon River) to 320µg/L in bottom waters of WHA. TN in surface waters were highest in the Gordon river with a median value of 270µg/L, and median values throughout the harbour proper were constant at 220µg/L, which is below the national default guideline value of 300µg/L for estuaries in the South East Australian Region.
TN in the bottom waters were highest for the WHA and North Harbour sites with median values of 320µg/L and 300µg/L respectively (i.e., at or above the national default guideline value). Median values for the Gordon River and Kelly Channel sites were similar to the surface values for these sites reflecting the well mixed nature, at least 50% of the time, of the water at these sites.

Total Nitrogen time series plots for surface waters
Total Nitrogen time series plots below reflect elevated nitrogen in surface waters of the Gordon River, and mild seasonality, winter elevations, throughout Macquarie Harbour.
TN collected from surface waters in the upper reaches of the Gordon River including a site above the confluence of the Franklin at the beginning of the sampling period (quarterly from Nov 2012 until Nov 2013) ranged in concentration from 230µg/L to 360µg/L. These values reflect the range of those sampled in the lower reaches of the Gordon reflecting Nitrogen entering the harbour from the riverine sources further up the catchment.

Elevated TN values in the Kelly Channel (mouth of harbour) correspond to periods of depressed salinity (less than 10PSU) consistent with a falling tide and/or high flow events from the Gordon bringing nutrient rich riverine water undiluted (by marine waters within the harbour) down the Western shoreline of the harbour to exit via the Kelly Channel. This pattern reflects the hydrodynamic circulation detailed in “Overview of Water Quality in Macquarie Harbour and Assessment of Risks due to Copper Levels” (Koehnken, 2005).

**Total Nitrogen time series plots for bottom waters**

TN collected from bottom waters in the upper reaches of the Gordon River including a site above the confluence of the Franklin at the beginning of the sampling period (quarterly from Nov 2012 until Nov 2013) ranged in concentration from 220µg/L to 350µg/L. These values are similar to the surface TN values reflecting the well mixed nature of the river at these sites and fall within the proposed guideline values for this catchment, i.e. high ecological value ecosystem the TN is 412µg/L and slightly to moderately disturbed ecosystems the TN is 394µg/L).
Total Nitrogen time series plots reflect elevated nitrogen in bottom waters of the World Heritage Area and the Northern Harbour. Site WHA4 had the greatest range in bottom waters of the WHA with a minimum TN of 240 µg/L to a maximum of 400 µg/L. In the Northern Harbour, site MH12 had the greatest range of TN with a minimum of 210 µg/L to a maximum value of 420 µg/L.
Total Kjeldahl Nitrogen (TKN)

TKN (Total Kjeldahl Nitrogen) is the sum of ammonia-nitrogen plus organically bound nitrogen but does not include nitrate-nitrogen or nitrite-nitrogen, it can provide a measure of the protein content of water. TKN though does not distinguish between the labile and refractory fractions of the organic nitrogen.

For the 2013-2016 period surface waters had the greatest range of median TKN values, from 180µg/L in the WHA region of the harbour to 220 µg/L at the site in the Gordon River.
Median TKN values in the bottom waters varied very little over this period with values of 190 µg/L at the Gordon River site and the balance of the harbour reporting medians of 200 µg/L. However, for this period, the greatest range of TKN occurred in the bottom waters of the WHA and North Harbour sites.
Total Kjeldahl Nitrogen time series plots for surface waters

The plots below present the TKN as time series over the length of the harbour for surface waters.

![Gordon River, Total Kjeldahl (N) ug/L (Surface Depths)](image1)

![WHA, Total Kjeldahl (N) ug/L (Surface Depths)](image2)
The elevated TKN values for the WHA and North Harbour sites in mid 2014 relate to river waters flooding through the harbour. This is confirmed by depressed salinity values for these sites with surface values less than 4PSU (the long term median is >7PSU - >9PSU for sites at similar locations, i.e., MH27 and MH12).

Nitrogen in the surface waters of all areas of the harbour is dominated by organic N (TKN) with a considerable contribution being made by flows from the Gordon river. A relatively small fraction (10-20%) of TN is composed of dissolved inorganic nitrogen (NOx and ammonia & ammonium) in surface waters.
Total Kjeldahl Nitrogen time series plots for bottom waters

The plots below present the TKN as time series over the length of the harbor for bottom waters.

Bottom waters in the WHA and North Harbour sites have a much greater proportion (30-40%) of NOx making up the nitrogen species. Whereas bottom waters of Kelly Channel and Gordon River sites are dominated by organic nitrogen similar to the surface waters.

Nitrate and Nitrite (NOx)

For the 2013-2016 period NOx levels were generally lower in surface waters than in bottom waters. This pattern is similar to that in other Tasmanian estuaries (DEP) where it is considered that Nitrate is taken up by primary production in the photic zone and released to bottom waters following the breakdown of organic matter in sediments. Also more significantly in low euphotic depth waters bacteria as decomposers use the carbon and nutrients as a source of sugars and protein and are integral to the carbon and nutrient cycles in the aquatic environment.

The nitrification process by nitrifying bacteria in marine (and freshwater) waters rapidly converts nitrite (NO$_2$) to nitrate (NO$_3$) resulting in the majority of NOx being composed of nitrate in this environment. The nitrogenous (and organic carbon) oxygen demand operating in oxic conditions is illustrated in the graph below where the oxygen is depleted moving through the water column for all site moving from North to South in the harbour. The significance of “fresh well oxygenated” marine recharge is also evident in this graph.
Organic carbon breakdown lowers the DO as carbon is incorporated into bacteria and released in part as carbon dioxide through respiration. In the anoxic conditions denitrifying bacteria would be converting nitrate to nitrite and nitrogen gas where nitrogen fixation would occur to convert to ammonium. Mineralization of the available nitrogen would also be occurring under anoxic conditions.

NOx in the surface waters ranged from a minimum of 2 µg/L in the North Harbour transect to a maximum of 69 µg/L at the Gordon River site. In bottom waters the range was greater with a minimum value of 7 µg/L recorded in the Kelly Channel and maximum values of 140 µg/L being observed in both the WHA and North Harbour transects.

Median values for NOx in surface waters were highest at the North Harbour sites (43 µg/L) and WHA (38 µg/L) and more than twice the median values observed over a period between 1995 and 1997 for similar sites of 18 µg/L and 11 µg/L respectively.
For bottom waters median NOx values were highest in the WHA and Northern Harbour areas (120 µg/L and 100 µg/L respectively). These levels were considerably higher than historic median values for similar sites of 58.5 µg/L (MH27,32,34) and 50 µg/L (MH11,12,13,14) respectively for the 1995 to 1997 period. The Gordon River and Kelly Channel sites had lower NOx levels in bottom waters (46.5 µg/L and 41 µg/L respectively), similar to values found in surface waters, possibly reflecting the well mixed nature of these sites.

NOx collected from waters in the upper reaches of the Gordon River including a site above the confluence of the Franklin at the beginning of the sampling period (quarterly from Nov 2012 until Nov 2013) were similar in scale to those at the Gordon River and Kelly Channel sites and ranged in concentration from 10µg/L to 42µg/L. The Kelly Channel median nitrate is not dissimilar to the proposed guideline values for coastal waters in the Franklin Bioregion, i.e., median and 80th%ile values for nitrate of 30.4µg/L and is 44.87µg/L, which illustrates the marine effects as expected.

Historic harbour values (1995-1997) and current riverine and Kelly Channel derived NOx values are similar in magnitude while NOx values for the bottom waters in the harbour proper are an order of magnitude greater. It appears that the source of NOx for the system must be within the harbour. The elevated NOx observed in the central harbour region must be entering the harbour from sources within the harbour in addition to those entering from either the Gordon River or marine waters (via the Kelly Channel).

Nitrate and Nitrite (N) time series plots for surface waters

Surface NOx time series plots detailing increasing levels are most pronounced in the WHA and to a lesser extent in the North Harbour transects. This would suggest generation of nitrate, movement of elevated NOx, and possible retention towards the southern region of the harbour.
Kelly Channel values show the influence of marine water intrusion on NOx values, where periods of decreased NOx correspond to elevated salinity (>30 PSU) levels. NOx levels, in general, are inversely related to salinity values. The low NOx corresponds to the tide gauge date which shows a rising water level in the harbour for this period.

Similarly, the DO levels over 2016 to 2017 in the WHA and Gordon River site, graphed below, illustrate the potential influence of lower DO harbour waters being displaced and moving from the southern harbour into the Gordon River. (The oxygenated riverine waters entering the harbour is also evident).
Nitrate and Nitrite (N) time series plots for bottom waters

Bottom water NOx time series plots, below, detailing a gradual increase in concentration over the period at both the WHA and North Harbour sites as well as the Gordon River site. NOx levels in bottom waters at the Gordon River site are related to salt water intrusion from the harbour proper as discussed above. The highest NOx value (110µg/L) occurring with a salinity of 23.4 PSU; the linear regression of Salinity/NOx for this site has an R² value of 0.67.

Bottom waters of the Kelly Channel has the lowest overall NOx values (median of 41µg/L) and doesn’t reflect this increasing trend but its greater range (7-58µg/L) may reflect the influence of marine waters through the opening at Hells Gates. These values are similar to the EPA Kelly Channel site (1-66µg/L) and in general agreement with the proposed guideline values for coastal waters in the Franklin Bioregion, i.e., median and 80th%ile values for nitrate of 30.4µg/L and 44.8µg/L respectively.
Ammonia and Ammonium (NH$_3$ + NH$_4^+$) – Total Ammonia

Ammonia and ammonium, i.e., total ammonia, are important nutrients for phytoplankton and bacteria involved in the nitrogen cycle. Elevated levels can cause algae blooms, increased primary production and decomposer populations, the proportions of which is dictated by the euphotic depth. All the measured ammonia in the harbour are below guideline values considered likely to cause toxic effects, e.g., at pH 8 the toxicant guideline value for total ammonia is 900µg/L.

For the 2013-2016 period ammonia and ammonium level was similar in surface and bottom waters of the well mixed sites in the Gordon River and Kelly Channel, with median values ranging from 11 µg/L to 14 µg/L.

In the harbour, WHA and central harbour sites, the median ammonia and ammonium levels in bottom waters were 5 µg/L and 6.6 µg/L respectively, approximately half of those in the surface waters (12 µg/L and 13 µg/L respectively). This is reflective of the N cycle, i.e. planktonic uptake and breakdown with bacterial nitrifiers converting ammonia to nitrate under oxic conditions, particulate organic nitrogen being formed, and nitrate to nitrogen gas or remineralized under anoxic conditions.
Ammonia and Ammonium (N) time series plots for surface waters

Time series plots below depict values for Ammonia and Ammonium in surface waters over the period.

These values are of a similar scale to those collected in the upper reaches of the Gordon that reported as a median of 14.5 µg/L for surface waters and values reported at Hells Gates of 10 µg/L.

Greater variation across the transect with site MH 14 (Liberty Point) differing from the other sites in this transect cannot at this stage be immediately explained as it does not appear to be related to salinity or any other parameter measured.

Ammonia and Ammonium (N) time series plots for bottom waters

Well mixed sites at either end of the harbour (Gordon River and Kelly Channel) have bottom ammonia/ammonium values similar to surface waters. These areas are turbulent and are not under oxygen stress. The very stable low levels of ammonia/ammonium in bottom waters of the harbour (WHA and Northern harbour sites) occur in the oldest and most stable part of the water body (estimated to be up to 6 month residence time) that also corresponds to areas of reduced dissolved oxygen.
The low DO and low ammonia/ammonium as discussed above is likely to be principally caused by planktonic organism such as heterotrophic (nitrifying) bacteria as part of the nitrogen cycle.

**Phosphorous**

Total Phosphorous (TP) is a measure of all forms of dissolved and particulate phosphorous found in water. TP mostly exists as phosphates, i.e. orthophosphates (reactive phosphates) and condensed phosphates (pyro, meta, and polyphosphates) representing the inorganic phosphorus fraction, and as the organic phosphate fraction.

For the 2013-2016 period the median TP values for surface waters were uniform across the harbour at 10µg/L which is below the national default guideline value for South East Australia estuaries of 30µg/L. The maximum (20µg/L) median TP values in bottom waters occurred in the WHA and North Harbour sites with Kelly Channel registering elevated levels (median of 16µg/L).

Dissolved Reactive Phosphorous (DRP) is a measure of the dissolved inorganic fraction of phosphorous and can be directly taken up by algae in primary production and bacteria where heterotrophic bacteria can compete for the inorganic P fraction.

As with Total Phosphorous median DRP values for surface waters were uniform across all areas of the harbour but at a lower level (3µg/L). The median DRP value in bottom waters of the harbour at the WHA and North Harbour sites is 6µg/L.
Both TP and DRP concentrations are highest in the harbour (WHA and North Harbour sites) and lowest in the riverine waters of the Gordon. It is also evident that the majority of phosphorous in the harbour, especially in the bottom waters of the WHA and North Harbour zones comprises other forms of phosphorous other than DRP. Any remobilization of phosphorus from sediments under anoxic/hypoxic conditions will also be available within the P cycle as inorganic phosphate. The decomposed organic phosphorus will be converted to inorganic phosphorus and available or remineralised. The remineralization of phosphorus proceeds as a function of the availability of the resource, the elemental requirements of the remineralizing bacteria, the lability of organic phosphorus resources, and environmental conditions. Changes in the ambient inorganic nitrogen:phosphorus ratio may modulate the rate of dissolved organic phosphorus production. Balancing this production is biotic decomposition, which occurs as microbes scavenge organic pools for essential elements. Dissolved organic phosphorus regenerated by bacteria can be taken immediately up by the same bacterial cell.

In earlier investigation into nutrient level in Macquarie Harbour conducted in 1995-1997 a number of samples were analysed for DRP at various depths in the harbour. The surface median value for WHA and North Harbour was 2µg/L while the bottom median value was 3µg/L. Comparing historic values to recent values there has been a harbour wide increase in DRP with the most significant elevation in DRP occurring in the bottom waters in both the Northern Harbour and WHA sites.