Healthy Harbour Watchers: Community-Based Water Quality Monitoring and Chemistry Education in Dunedin

Andrew Innes,[a] Steven A. Rusak,[b] Barrie M. Peake[b] and David S. Warren[b]

[a]John McGlashan College and [b]Department of Chemistry, Otago University, PO Box 56, Dunedin
(email: *stever@chemistry.otago.ac.nz*)

Introduction

Healthy Harbour Watchers is a community-based programme that enables students and volunteers to perform independent investigations into chemical and biological processes in Otago Harbour, while also contributing to an ongoing water-quality data set. The programme began in 2004 when one of the authors (AI) received a Science, Mathematics and Technology Teacher Fellowship from RSNZ. The intention of the Healthy Harbour Watchers programme is to develop community knowledge and skills related to the chemical analysis of seawater. To that end, the programme has involved hundreds of volunteers, including high-school and university students, children, parents, and members of the general public in the collection and analysis of water samples from Otago Harbour over the past six years. The students and volunteers meet at the Otago University Chemistry Department and then work in groups to collect data and water samples from nine standard sites around Otago Harbour using the latitude/longitude data to accurately locate their allocated site (Table 1). Temperature, salinity, pH, and dissolved O_2 are measured in the field prior to the samples being brought to the Chemistry Department where students and volunteers determine concentrations of dissolved reactive phosphorus (DRP), nitrate/nitrite nitrogen (NNN), chlorophyll-*a* (chl-*a*), dissolved O_2, and counts of *Enterococci* bacteria using a suite of spectrophotometric, titrimetric, and microbiological techniques.

Table 1. Latitude and longitude positions of the Healthy Harbour Watchers' nine standard sampling sites.

Site No.	Name	Latitude/Longitude
1	Pulling Point	45° 47.720'S 170° 39.385'E
2	Back Beach-Port Chalmers	45° 49.089'S 170° 37.553'E
3	Mussel Bay-Port Chalmers	45° 49.249'S 170° 36.958'E
4	Ravensbourne Boat Club	45° 52.069'S 170° 32.978'E
5	Leith River Mouth	45° 52.300'S 170° 31.555'E
6	MacAndrew Bay Marina	45° 52.150'S 170° 35.710'E
7	MacAndrew Bay Stormwater Outfall	45° 52.175'S 170° 35.795'E
8	Sommerville Creek	45° 53.554'S 170° 31.680'E
9	Andersons Bay Outlet	45° 53.536'S 170° 31.233'E

The Healthy Harbour Watchers programme allows students and volunteers to perform independent investigations into water-quality parameters using a range of quantitative analysis methods. Students and volunteers are encouraged to design their own experiments and think independently to solve problems in a laboratory setting. Teachers and experienced volunteers give guidance about the sort of experiments that might be the most useful or appropriate. Not every student performs every analysis, but at the end of each session, all of the participants work together to assemble their data into a meaningful report, which is archived for future reference. The results of all the analyses performed are stored in Excel spreadsheets. The students and volunteers are introduced to a range of instrumental techniques for chemical analysis of natural water while working in a laboratory-centred learning environment at the University of Otago.

The programme provides the opportunity for analysis of water samples from several standard sampling sites six times per year, with the analyses having produced sufficient information to define a baseline for water quality in the harbour on the basis of the concentrations of nutrients, dissolved oxygen, and *Enterococci* counts. Because sampling and analyses are performed consistently over the course of each year, the data can be used also to answer questions about spatial and temporal trends in water quality parameters. As the programme continues, this collection of experimental results will provide an increasingly valuable record that may be used for development of a nutrient-based predictive model for water quality in our harbour, and to inform local government, the general public, and other stakeholders interested in the more effective management of Dunedin's water resources. Herein, data collected by the Healthy Harbour Watchers during the 2009 calendar year is presented as it demonstrates the synergy between community-based water quality monitoring and chemistry education in Dunedin.

Sampling Sites and Methods of Analysis

Nine standard sampling sites around Otago Harbour were selected (see Fig. 1 and Table 1) to represent a cross section of the types of water found within the harbour that range from pristine seawater in the lower harbour at Pulling Point, to terrestrially-influenced urban runoff in some areas of the upper harbour. Students and volunteers use Yellow Springs Instruments model 556 digital handheld multi-probe meters to collect information about temperature, salinity, and dissolved O_2 in the field. They then corroborate their field readings using a Mohr-Knudsen titration technique for salinity and a modified Winkler titration for dissolved oxygen.[1] The measurement of pH is by use of battery-powered pH meters, which the students calibrate using standard buffer solutions.

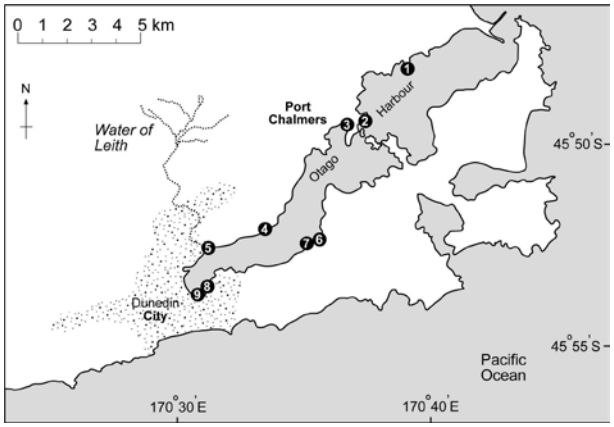

Fig. 1. Otago Harbour showing the locations of the Healthy Harbour Watchers' standard sampling sites (map designed by Lisa Bucke); the latitude/longitude of the sites appear in Table 1.

Concentrations of dissolved reactive phosphorus (DRP) are determined from the reaction of ammonium molybdate with inorganic phosphate in acidified samples and subsequent reduction of the complex to molybdenum blue. The optical density of the complex is determined by absorbance at 885 nm, and is directly proportional to the concentration of DRP in the original sample.[2] Concentrations of nitrate/nitrite nitrogen (NNN) are determined by first reducing nitrate to nitrite using a copper-cadmium column, followed by diazotisation of nitrite and subsequent formation of a pink azo dye, which is quantified by optical absorbance at 543 nm and is proportional to the sum of the concentrations of nitrate and nitrite ions present in the original sample.[3] Concentrations of chlorophyll-*a* in the water samples are determined by spectrophotometric analysis of the homogenate of material filtered from a known volume of sample water and extracted into acetone.[3] This is often the students' first experience with spectrophotometric analysis, and it provides an opportunity to introduce the Beer-Lambert Law and to explain the operation of an absorbance spectrophotometer. Concentrations of *Enterococci* are determined using a two-step membrane filtration method.[4] This microbiological analysis exposes the students to the concept of sterile techniques and introduces basic concepts related to microbial culture. Although the students do not prepare the growth medium themselves, they are responsible for filtering the water samples, aseptically introducing the filter membrane to the growth medium, and counting the colonies after a 48 hour incubation period.

2009 Results and Discussion

Temperature

Students and volunteers made 49 measurements of water temperature during the 2009 programme (Fig. 2). Temperature serves as a broad indicator of water quality, and has a direct bearing on chemical and biological processes that occur in the harbour, including nutrient cycling, and the population and distribution cycles of aquatic species. The minimum temperature measured in Otago Harbour was 7.5 C° at the mouth of the Leith River (site 5) on 23 May 2009, while the maximum temperature was 15.5 C° at the same site on 12 December (day 346). The mean of all of the temperature measurements was 10.8 C° and the data display the expected seasonal pattern and are shown in Fig. 2.

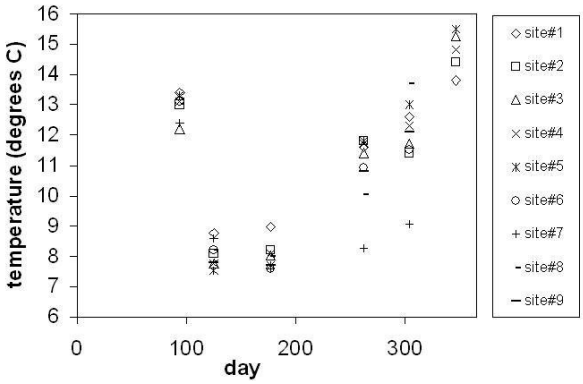

Fig. 2. Temperature variation at the 9 sites during 2009; samples were collected and analysed on 4 Apr, 23 May, 26 Jun, 19 Sep, 31 Oct, and 12 Dec 2009.

Salinity

Salinity in Otago Harbour fluctuates owing to rainfall, river flow, and tidal cycles. Salinity is expressed without units using the practical salinity scale.[5] The measured salinities ranged from 0.16 in MacAndrew Bay Stormwater (site 7) on 31 October (day 304) to 33.6 at Pulling Point (site 1) on 12 December (day 346) (Fig. 3). The vast majority of the samples had salinities between 29 and 33. However, samples collected from the mouth of the Leith River (site 5), MacAndrew Bay Stormwater Outfall (site 7), Sommerville Creek (site 8) and Anderson's Bay Outlet (site 9) sometimes had decreased salinity because of the proximity of the sampling sites to freshwater inputs.

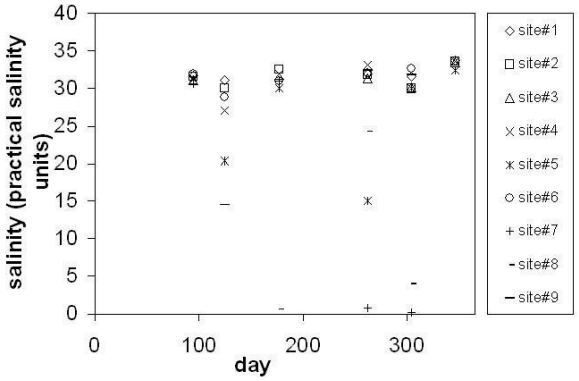

Fig. 3. Salinity variation at each site during 2009.

pH

In total, 37 pH measurements were made during 2009. Logistical constraints and limited availability of equipment meant that it was not possible to measure every parameter at every site during every meeting of the Watchers. However, all of the pH measurements recorded during 2009 are shown in Fig.4 and all of the measured pH values were within the guideline range of 6.5 to 9 with the single exception of the sample collected from the MacAndrew Bay Stormwater Outfall (site 7) on 31 October (day 304), which had a pH of 9.13. It is interesting to note that pH values appeared to decrease in response to the heavy rain event that occurred on 23 May (day 125).

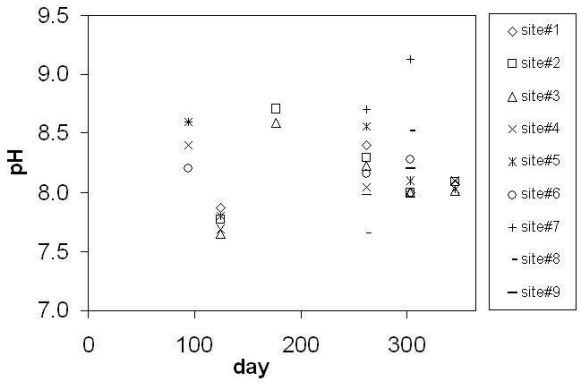

Fig. 4. pH variation at each site during 2009; the decrease on 23 May (day 125) is a result of heavy rain.

Dissolved Oxygen

Dissolved O_2 concentrations are an important indicator of eutrophication. When concentrations become depleted, the likelihood of algal blooms increases and the water becomes uninhabitable for fish and other heterotrophic organisms; the results appear in Fig. 5.

All of the dissolved O_2 concentrations measured in Otago Harbour were above 7 mg/L. Furthermore, no dead fish or dense algal blooms, which can be evidence of anoxia, were observed in any of the samples. Occasionally, samples collected from the mouth of the Water of Leith (site 5) and from the MacAndrew Bay Stormwater Outfall (site 7) were supersaturated with O_2, probably caused by turbulence resulting in entrainment of air into the water.

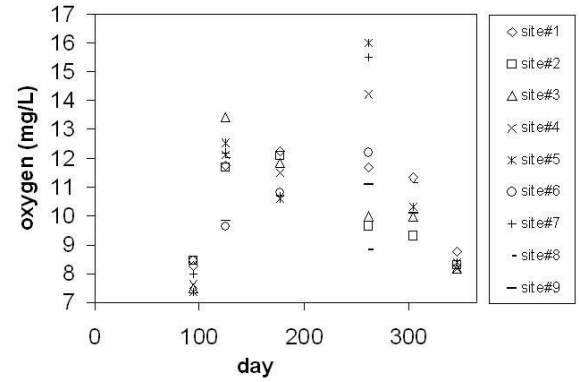

Fig. 5. Dissolved O_2 variation at each site during 2009.

Dissolved Reactive Phosphorus

Concentrations of DRP ranged from a maximum of 5.15 µM in Sommerville Creek (site 8) on 23 May (day 125), when the sample was collected during a severe rain event, to a minimum of 0.33 µM at Pulling Point (site 1) in the lower harbour on 12 December (day 346). Concentrations of DRP always exceeded the guideline value of 0.97 µM in the MacAndrew Bay Stormwater Outfall (site 7) and in Sommerville Creek (site 8), and occasionally exceeded the guideline value at all of the other sampling sites, with the exception of Pulling Point (Site 1) where the maximum measured concentration was 0.84 µM.

Phosphorus is the main cause of eutrophication in estuaries and is frequently a key indicator of water quality deterioration. Because phosphorus is often the limiting nutrient for plant growth in estuaries, even relatively small inputs of it can lead to algal blooms that, upon dying and decomposing, deplete oxygen to levels that can threaten aquatic life. A guideline value of 0.97 µM dissolved reactive phosphorus has been established for the Ruamahanga River near Wellington,[6] consistent with the UN Economic Commission for Europe and The Ontario Ministry of Environment and Energy guideline concentration values of 0.81 to 0.97 µM for phosphorus in surface water. The Healthy Harbour Watchers use a guideline value of 0.97 µM dissolved reactive phosphorus in surface water, with which the data from the sites are compared in Fig. 6. Much of the phosphorus present in estuarine waters is adsorbed on to particles and thereby sequestered from the dissolved phase. As a result, soils act as reservoirs of phosphorus and restrict the immediate impact of phosphorus inputs. However, when phosphorus-rich sediment is re-suspended, for example during a severe weather event, particle-adsorbed phosphorus may redissolve, leading to elevated concentrations of dissolved phosphorus in the water.

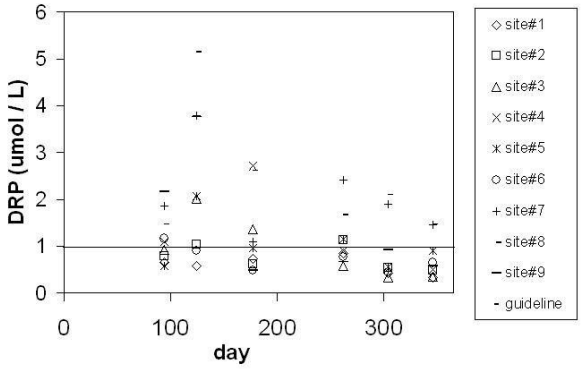

Fig. 6. Dissolved reactive phosphorus variation at each site during 2009.

Nitrate/Nitrite Nitrogen

Our programme has set a guideline concentration of 11.3 µM nitrogen present as nitrate and nitrite (NNN), consistent with the ANZ Environment and Conservation Council trigger value.[7] The measured concentrations of NNN varied from 0.34 µM to 63.4 µM (Fig. 7) and of the 52 samples analysed, 15 had concentrations of NNN above the guideline value. Samples collected from the mouth of the Water of Leith (site 5) and from the MacAndrew Bay Stormwater Outfall (site 7) consistently had concentrations higher than the guideline value.

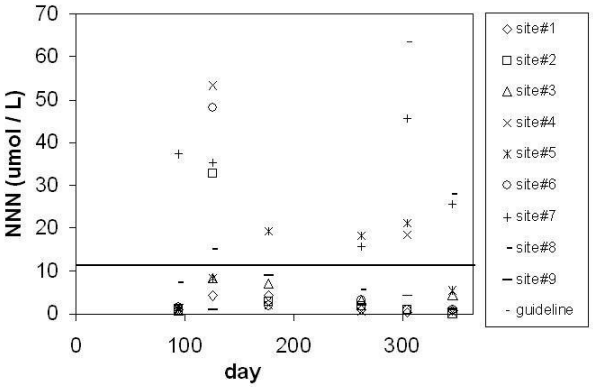

Fig. 7. Nitrate/nitrite nitrogen variation at each site during 2009.

*Chlorophyll-*a

The measured chl-*a* concentrations were below 4 µg/L with two exceptions, both of which occurred on 23 May (day 125) when the MacAndrew Bay Stormwater Outfall (site 7) was 15.2 µg/L, and that at Mussel Bay, Port Chalmers (site 3) was 7.80 µg/L (Fig. 8). While the concentration of 4 µg/L is not a benchmark concentration or trigger value per se, it is a convenient baseline value for chl-*a* concentrations in Otago Harbour, against which students and volunteers may compare their data to assist with the identification of anomalous measurements. During the 23 May (day 125) sampling trip, it is likely that heavy rain and wind suspended solids in the water that may have interfered with the analysis, leading to anomalously high concentrations of chl-*a* in the samples. Overall, the measured concentrations of chl-*a* ranged from a maximum of 15.2 µg/L in the MacAndrew Bay Stormwater Outfall (site 7) during the 23 May (day 125) sampling trip to a minimum of 0.26 µg/L at the MacAndrew Bay Marina (site 6) during the December sampling on day 346.

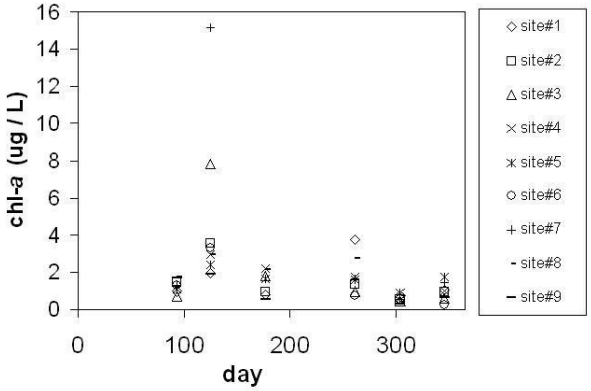

Fig. 8. Measured chlorophyll-*a* concentration variations at each site during 2009.

Enterococci Counts

Enterococci are bacteria often found in the feces of humans and other warm blooded animals.[4] Not all strains of *Enterococci* are related to fecal pollution, but the presence of *Enterococci* in marine water is a widely accepted indicator of the possible presence of pathogens.[4] The guideline for *Enterococci* concentration was set as 140 colonies/100 mL, which is the same as the recreational water quality guideline used by the Otago Regional Council.[8] The measured concentrations exceeded this guideline in only three out of the 35 samples that were analysed (Fig. 9). The sample from Sommerville Creek (site 8) and the sample from the Leith River Mouth (site 5) had high *Enterococci* counts during the May sampling trip (day 125), which coincided with a heavy rain event. In addition, the sample from Sommerville Creek contained 176 Enterococci colonies/100 mL on 31 October 2009 (day 304).

Conclusion

Healthy Harbour Watchers guideline values for concentrations of nutrients and bacteria are not intended to be applied directly as regulatory criteria or limits, but are factors for students and volunteers to consider when making decisions about future investigations. While the need to define guideline values for nutrients is debatable,[7]

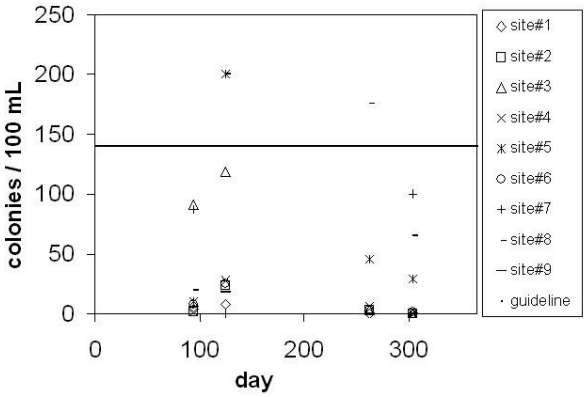

Fig. 9. *Enterococci* count variation at each site during 2009; samples with colonies too numerous to measure are shown as 200 colonies/100 mL.

some indication of nutrient concentrations that constitute a threat are needed in order to assist students with data interpretation and experimental design. When students and volunteers measure values that are within the range prescribed by the guidelines, they are monitored and recorded, and when the measured values are outside of the guidelines, students are encouraged to perform more detailed investigations into the reasons for the deviations observed and suggest possible remedies.

There are many anthropogenic sources of nutrients around Otago Harbour. Wastewater discharges, terrestrial runoff, fertilizers, and atmospheric deposition can all contribute to elevated concentrations of nitrate and dissolved reactive phosphorus. The data collected by us generally suggest that further site-specific investigations are necessary to determine if special action is required to limit nutrient and bacterial input into Otago Harbour. No evidence of anoxia or excessive eutrophication was found in the data reported here, and chl-*a* concentrations suggest that excessive algal growth did not occur at any of the sampling sites. However, concentrations of nitrate/nitrite nitrogen and dissolved reactive phosphorus were frequently above the guideline values, particularly at the MacAndrew Bay Stormwater Outfall and at the mouth of the Water of Leith, where terrestrial inputs and anthropogenic sources are likely to have influenced nutrient concentrations.

Most importantly, the Healthy Harbour Watchers programme has transfered chemistry knowledge and analytical skills to students and volunteers, while also providing information about baseline water quality in the harbour. The students are encouraged to perform independent investigations into water quality parameters and, throughout, the Chemistry Department provide them with access to a range of quantitative analysis methods and practical experiences that are not available in high school laboratories. In the future, the Healthy Harbour Watchers programme hopes to involve students and volunteers in the development of a nutrient-based predictive model for water quality in Otago Harbour continue to engage them in the collection and analysis of water samples from the harbour.

Acknowledgements

We thank Otago area school teachers, students, volunteers and

helpers for making the programme possible, especially David Patchett, Murray Vickers, and Kate Gnoth for continuing support. We are indebted to Ian Billinghurst, Rob Alumbaugh, and Ben Durrant for laboratory assistance. The RSNZ is thanked for its Science, Mathematics and Technology Teacher Fellowship (to AI).

References

1. Carpenter, J.H. *Limnol. Oceanogr.* **1965**, *10*, 141-143.
2. Murphy, J.; Riley, J.P. *Anal. Chim. Acta* **1962**, *27*, 31-36.
3. Parsons, T.R.; Maitra, Y.; Lalli, C.M. *A Manual of Chemical and Biological Methods for Seawater Analysis* Pergamon: New York, 1984.
4. *Levin*, M.A.; *Fischer*, J.R.; *Cabelli*, V.J. *Appl. Microbiol.* **1975**, *30, 66*–71.
5. Lewis, E. L. *Marine Geodesy* **1982**, *5*, 350-357.
6. Hickey, C.W.; Norton, N.; Broekhuizen, N. *Proposed dissolved reactive phosphorus guidelines for the Ruamahanga River,* NIWA: Wellington, 2004.
7. ANZEE & ARMCANZ *Australian and New Zealand guidelines for fresh and marine water quality,* Canberra, 2000.
8. *Recreational Water Quality Annual Monitoring Summary 2008/09,* Otago Regional Council, 2009.