

# Water Quality in the Marlborough Sounds

Annual Monitoring report July 2014-June 2015

*Prepared for Marlborough District Council*

*June 2015*

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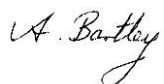
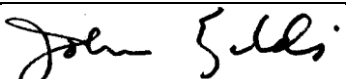
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NIWA CLIENT REPORT No: HAM2015-094  
Report date: August 2015  
NIWA Project: MDC15201

Quality Assurance Statement		
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## Contents

<b>Executive summary .....</b>	<b>11</b>
<b>1 Introduction .....</b>	<b>12</b>
1.1 Water Quality Standards (for trophic status) .....	13
<b>2 The monitoring program .....</b>	<b>16</b>
2.1 Monitoring locations & methods.....	16
2.2 CTD data.....	21
<b>3 Results (Queen Charlotte Sound).....</b>	<b>23</b>
3.1 Temperature .....	23
3.2 Salinity.....	26
3.3 Dissolved oxygen .....	30
3.4 Suspended inorganic solids.....	34
3.5 Turbidity.....	35
3.6 Dissolved reactive phosphorus .....	36
3.7 Total dissolved phosphorus .....	37
3.8 Dissolved organic phosphorus .....	38
3.9 Dissolved reactive silicon .....	39
3.10 Total dissolved nitrogen .....	40
3.11 Nitrate .....	41
3.12 Ammoniacal nitrogen .....	42
3.13 Dissolved organic nitrogen .....	43
3.14 Particulate nitrogen .....	44
3.15 Particulate carbon.....	45
3.16 PN:PC .....	46
3.17 Total nitrogen .....	47
3.18 Volatile Suspended Solids .....	48
3.19 Chlorophyll.....	49
3.20 Algal carbon .....	50
3.21 Zooplankton carbon.....	51
3.22 Elemental ratios .....	52
3.23 PAR attenuation coefficient.....	53
3.24 Secchi disk depth .....	53

<b>4</b>	<b>Results (Pelorus Sound)</b> .....	<b>56</b>
4.1	Temperature .....	56
4.2	Salinity.....	59
4.3	Dissolved oxygen .....	63
4.4	Suspended inorganic solids.....	68
4.5	Turbidity.....	69
4.6	Dissolved reactive phosphorus.....	70
4.7	Total dissolved phosphorus .....	71
4.8	Dissolved organic phosphorus.....	72
4.9	Dissolved reactive silicon .....	73
4.10	Total dissolved nitrogen .....	74
4.11	Nitrate .....	75
4.12	Ammoniacal nitrogen .....	76
4.13	Dissolved organic nitrogen .....	77
4.14	Particulate nitrogen .....	78
4.15	Particulate carbon.....	79
4.16	PN:PC .....	80
4.17	Total nitrogen .....	81
4.18	Volatile Suspended Solids.....	82
4.19	Chlorophyll.....	83
4.20	Algal carbon .....	84
4.21	Zooplankton carbon.....	85
4.22	Elemental ratios.....	86
4.23	Secchi disk depth .....	87
<b>5</b>	<b>Results (Port Gore)</b> .....	<b>89</b>
5.1	CTD temperature profiles .....	89
5.2	CTD salinity profiles .....	89
5.3	CTD oxygen profiles .....	90
5.4	Other water quality characteristics .....	91
5.5	Algal carbon .....	92
<b>6</b>	<b>Data exclusions and other matters</b> .....	<b>93</b>
<b>7</b>	<b>Conclusions &amp; Recommendations</b> .....	<b>98</b>
7.1	Data distributions and Flag values .....	98

7.2	Dissolved oxygen and NZKS management protocols.....	99
7.3	Revisions to sampling patterns.....	100
7.4	Tory Channel.....	100
7.5	Handheld temperature, salinity and dissolved oxygen data .....	100
7.6	CTD profiling .....	101
7.7	Secchi Disk .....	101
<b>8</b>	<b>Acknowledgements .....</b>	<b>102</b>
<b>9</b>	<b>References.....</b>	<b>103</b>
<b>Appendix A</b>	<b>Methods for phytoplankton and zooplankton counts .....</b>	<b>106</b>
<b>Appendix B</b>	<b>Probability distributions in the Queen Charlotte water-quality data .....</b>	<b>108</b>
<b>Appendix C</b>	<b>Probability distributions in the Pelorus water-quality data .....</b>	<b>123</b>

#### Tables

Table 1-1:	Examples of coastal water-quality thresholds and/or standards relevant to the Marlborough Sounds.	14
Table 2-1:	Characteristics measured in each water-quality sample.	18
Table 6-1:	Summary of sampling records which are considered dubious and of records which have been rejected.	93
Table A-1:	Cell count accuracy.	106
Table A-2:	Microscope calibration.	107

#### Figures

Figure 2-1:	Locations of the Marlborough District Council sampling stations.	18
Figure 3-1:	Queen Charlotte: Near surface water temperature measured with a hand-held probe at each of the five water quality sampling stations.	23
Figure 3-2:	Contour plots of the evolving depth profiles of temperature through time at the Queen Charlotte and Tory stations.	26
Figure 3-3:	Queen Charlotte: Salinity measured at sea with a hand-held probe at 1 m depth (black circles) and in water-samples returned to the laboratory (red circles: near surface (1m or depth averaged to 15 m); blue circles: near-bed). Different instruments were used to measure salinity at sea and in the laboratory.	27
Figure 3-4:	Contour plots of the evolving depth profiles of salinity through time at the Queen Charlotte and Tory stations.	29
Figure 3-5:	Dissolved oxygen measured at one metre below the sea-surface at the five Queen Charlotte water-quality monitoring stations.	31

Figure 3-6:	Contour plots of the evolving depth profiles of oxygen saturation through time at the Queen Charlotte and Tory stations.	33
Figure 3-7:	Concentrations of suspended inorganic solids measured in the near-surface water-samples of the five Queen Charlotte Sound/Tory Channel stations.	34
Figure 3-8:	Near-surface turbidity measured at the five Marlborough District Council water quality monitoring sites in Queen Charlotte/Tory Channel.	35
Figure 3-9:	Time-series of dissolved reactive phosphorus measured near the surface (red) and near the seabed (blue) at the MDC sampling sites in Queen Charlotte Sound.	36
Figure 3-10:	Total dissolved near-surface (red) and near-bed (blue) phosphorus measured at the five Marlborough District Council stations in Queen Charlotte Sound.	37
Figure 3-11:	Inferred near-surface (red) and near-bed (blue) dissolved organic phosphorus (TDP-DRP) at the five Marlborough District Council water quality sites in Queen Charlotte Sound.	38
Figure 3-12:	Dissolved reactive silicon concentrations near-surface (red) and near-bed (blue) at the five Marlborough District Council water quality stations in Queen Charlotte Sound.	39
Figure 3-13:	Total dissolved nitrogen near-surface (red) and near-bed (blue) measured at the five Marlborough District Council water-quality stations in Queen Charlotte Sound.	40
Figure 3-14:	Nitrate concentrations near-surface (red) and near-bed (blue) measured at the five Marlborough District Council water-quality stations in Queen Charlotte Sound.	41
Figure 3-15:	Ammoniacal nitrogen near-surface (red) and near-bed (blue) measured at the five Marlborough District Council water-quality stations in Queen Charlotte Sound.	42
Figure 3-16:	Inferred dissolved organic nitrogen concentrations near-surface (red) and near-bed (blue) at the five Marlborough District Council stations in Queen Charlotte Sound.	43
Figure 3-17:	Particulate nitrogen near-surface (red) and near-bed (blue) at the five Marlborough District Council monitoring stations in Queen Charlotte Sound.	44
Figure 3-18:	Particulate carbon near-surface (red) and near-bed (blue) at the five Marlborough District Council monitoring stations in Queen Charlotte Sound.	45
Figure 3-19:	PN:PC ratios in near-surface (red) and near-bed (blue) samples at the Marlborough District Council sampling sites in Queen Charlotte Sound.	46
Figure 3-20:	Total nitrogen in near-surface (red) and near-bed (blue) water measured at the five Marlborough District Council sampling sites in Queen Charlotte Sound.	47
Figure 3-21:	Volatile suspended solids concentrations measured in the near-surface waters at the five Marlborough District Council sites in Queen Charlotte Sound.	48
Figure 3-22:	Chlorophyll concentrations measured near-surface (red) and near-bed (blue) at the five Marlborough District Council stations in Queen Charlotte Sound.	49

Figure 3-23:	Phytoplankton carbon concentration from cell counts and cell dimensions at the Marlborough District Council stations (near surface water samples) in Queen Charlotte Sound.	50
Figure 3-24:	Zooplankton biomass inferred from counts and dimensions at the five Marlborough District Council sites (near surface water samples) in Queen Charlotte Sound.	51
Figure 3-25:	Ratios of dissolved inorganic nutrients measured near-surface (red) and near-bed (blue) at each site in Queen Charlotte Sound.	52
Figure 3-26:	Secchi disk depth measured at the five sites in Queen Charlotte Sound and Tory Channel.	54
Figure 3-27:	PAR attenuation coefficients inferred using the relationship described in Kirk (left panels) and the data of Vincent et al. (right panels in Queen Charlotte Sound).	55
Figure 4-1:	Near surface water temperature measured with a hand-held probe at each of the seven Marlborough District Council Pelorus water quality sampling stations.	56
Figure 4-2:	Contour plots of evolving depth profiles of temperature through time at the Pelorus stations.	59
Figure 4-3:	Salinity measured at the seven Marlborough District Council sites within Pelorus. A hand-held probe was used at 1 m depth (black circles) and in water-samples were returned to the laboratory (red circles: near surface (1m or depth averaged to 15 m); blue circles: near-bed). Different instruments were used to measure salinity at sea and in the laboratory.	60
Figure 4-4:	Contour plots of evolving depth profiles of salinity through time at the Pelorus stations.	63
Figure 4-5:	Dissolved oxygen measured at one metre below the sea-surface at the seven Marlborough District Council Pelorus water-quality monitoring stations.	64
Figure 4-6:	Contour plots of evolving depth profiles of oxygen saturation through time at the Pelorus stations.	67
Figure 4-7:	Concentrations of suspended inorganic solids measured in the near-surface water-samples of the seven Marlborough District Council Pelorus stations.	68
Figure 4-8:	Near-surface turbidity measured at the seven Marlborough District Council water quality monitoring sites in Pelorus.	69
Figure 4-9:	Time-series of dissolved reactive phosphorus measured near surface (red) and near bed (blue) at the seven Marlborough District Council Pelorus sampling sites.	70
Figure 4-10:	Total dissolved near-surface (red) and near-bed (blue) phosphorus measured at the seven Marlborough District Council Pelorus stations.	71
Figure 4-11:	Inferred near-surface (red) and near-bed (blue) dissolved organic phosphorus (TDP-DRP) at the seven Marlborough District Council Pelorus water quality sites.	72
Figure 4-12:	Dissolved reactive silicon concentrations near-surface (red) and near-bed (blue) at the seven Marlborough District Council Pelorus water quality stations.	73
Figure 4-13:	Total dissolved nitrogen near-surface (red) and near-bed (blue) measured at the seven Marlborough District Council Pelorus water-quality stations.	74

Figure 4-14:	Nitrate concentrations near-surface (red) and near-bed (blue) measured at the seven Marlborough District Council Pelorus water-quality stations.	75
Figure 4-15:	Ammoniacal nitrogen near-surface (red) and near-bed (blue) measured at the seven Marlborough District Council Pelorus water-quality stations.	76
Figure 4-16:	Inferred dissolved organic nitrogen concentrations near-surface (red) and near-bed (blue) at the seven Marlborough District Council Pelorus stations.	77
Figure 4-17:	Particulate nitrogen near-surface (red) and near-bed (blue) at the seven Marlborough District Council Pelorus monitoring stations.	78
Figure 4-18:	Particulate carbon near-surface (red) and near-bed (blue) at the seven Marlborough District Council Pelorus monitoring stations.	79
Figure 4-19:	PN:PC ratios in near-surface (red) and near-bed (blue) samples at the seven Marlborough District Council Pelorus sampling sites.	80
Figure 4-20:	Total nitrogen in near-surface (red) and near-bed (blue) water measured at the seven Marlborough District Council Pelorus sampling sites.	81
Figure 4-21:	Volatile suspended solids concentrations measured in the near-surface waters at the seven Marlborough District Council Pelorus sites.	82
Figure 4-22:	Chlorophyll concentrations measured near-surface (red) and near-bed (blue) at the seven Marlborough District Council Pelorus stations.	83
Figure 4-23:	Phytoplankton carbon concentration from cell counts and cell dimensions at the seven Marlborough District Council Pelorus stations (near surface water samples).	84
Figure 4-24:	Zooplankton biomass inferred from counts and dimensions at the seven Marlborough District Council Pelorus sites (near surface water samples).	85
Figure 4-25:	Ratios of dissolved inorganic nutrients measured near-surface (red) and near-bed (blue) at each MDC Pelorus site.	86
Figure 4-26:	Secchi disk depth measured in Pelorus Sound at the seven Marlborough District Council stations.	87
Figure 4-27:	PAR attenuation coefficients in Pelorus Sound inferred using the relationship described in Kirk (left panels) and the data of Vincent et al. (right panels).	88
Figure 5-1:	Contour plots of the evolving depth profiles of temperature through time at the Cook Strait mouth of Port Gore.	89
Figure 5-2:	Contour plots of evolving depth profiles of salinity through time at the Cook Strait mouth of Port Gore.	89
Figure 5-3:	Contour plots of evolving depth profiles of dissolved oxygen through time at the Cook Strait Mouth of Port Gore.	90
Figure 5-4:	Water quality characteristics measured at the Cook Strait mouth of Port Gore from the New Zealand King Salmon Ltd, Marlborough District Council and NIWA sampling programmes.	91
Figure 5-5:	Time-series of taxon-specific, near-surface phytoplankton biomass concentration measured at the Port Gore station in the NZKS, MDC and NIWA time-series.	92
Figure 7-1:	Scatter plots illustrating the relationships between Secchi disk depth and candidate water-quality properties that have been measured.	102



Figure B-1:	Empirical probability density distributions for the concentration of near-surface suspended inorganic solids in Queen Charlotte Sound/Tory Channel.	108
Figure B-2:	Empirical probability density distributions for near-surface turbidity in Queen Charlotte Sound/Tory Channel.	109
Figure B-3:	Empirical probability density distributions for near-surface and near-bed dissolved reactive phosphorus in Queen Charlotte Sound/Tory Channel.	110
Figure B-4:	Empirical probability density distributions for near-surface and near-bed total dissolved phosphorus in Queen Charlotte Sound/Tory Channel.	111
Figure B-5:	Empirical probability density distributions for near-surface and near-bed dissolved organic phosphorus in Queen Charlotte Sound/Tory Channel.	112
Figure B-6:	Empirical probability density distributions for near-surface and near-bed dissolved reactive silicon in Queen Charlotte Sound/Tory Channel.	113
Figure B-7:	Empirical probability density distributions for near-surface and near-bed total dissolved nitrogen in Queen Charlotte Sound/Tory Channel.	114
Figure B-8:	Empirical probability density distributions for near-surface and near-bed nitrate in Queen Charlotte Sound/Tory Channel.	115
Figure B-9:	Empirical probability density distributions for near-surface and near-bed ammoniacal nitrogen in Queen Charlotte Sound/Tory Channel.	116
Figure B-10:	Empirical probability density distributions for near-surface and near-bed dissolved organic nitrogen in Queen Charlotte Sound/Tory Channel.	117
Figure B-11:	Empirical probability density distributions for near-surface and near-bed particulate nitrogen (or particulate organic nitrogen in cases where that was measured instead) in Queen Charlotte Sound/Tory Channel.	118
Figure B-12:	Empirical probability density distributions for near-surface and near-bed particulate carbon (or particulate organic carbon where that was measured instead) in Queen Charlotte Sound/Tory Channel.	119
Figure B-13:	Empirical probability density distributions for near-surface and near-bed total nitrogen in Queen Charlotte Sound/Tory Channel.	120
Figure B-14:	Empirical probability density distributions for near-surface volatile suspended solids in Queen Charlotte Sound/Tory Channel.	121
Figure B-15:	Empirical probability density distributions for near-surface and near-bed chlorophyll concentration in Queen Charlotte Sound/Tory Channel.	122
Figure C-1:	Empirical probability density distributions for the concentration of near-surface suspended inorganic solids in Pelorus Sound.	123
Figure C-2:	Empirical probability density distributions for near-surface turbidity in Pelorus Sound.	124
Figure C-3:	Empirical probability density distributions for near-surface and near-bed dissolved reactive phosphorus in Pelorus Sound.	125
Figure C-4:	Empirical probability density distributions for near-surface and near-bed total dissolved phosphorus in Pelorus Sound.	126
Figure C-5:	Empirical probability density distributions for near-surface and near-bed dissolved organic phosphorus in Pelorus Sound.	127
Figure C-6:	Empirical probability density distributions for near-surface and near-bed dissolved reactive silicon in Pelorus Sound.	128
Figure C-7:	Empirical probability density distributions for near-surface and near-bed total dissolved nitrogen in Pelorus Sound.	129

Figure C-8:	Empirical probability density distributions for near-surface and near-bed nitrate in Pelorus Sound.	130
Figure C-9:	Empirical probability density distributions for near-surface and near-bed ammonical nitrogen in Pelorus Sound.	131
Figure C-10:	Empirical probability density distributions for near-surface and near-bed dissolved organic nitrogen in Pelorus Sound.	132
Figure C-11:	Empirical probability density distributions for near-surface and near-bed particulate nitrogen (or particulate organic nitrogen in cases where that was measured instead) in Pelorus Sound.	133
Figure C-12:	Empirical probability density distributions for near-surface and near-bed particulate carbon (or particulate organic carbon where that was measured instead) in Pelorus Sound.	134
Figure C-13:	Empirical probability density distributions for near-surface and near-bed total nitrogen in Pelorus Sound.	135
Figure C-14:	Empirical probability density distributions for near-surface volatile suspended solids in Pelorus Sound.	136
Figure C-15:	Empirical probability density distributions for near-surface and near-bed chlorophyll concentration in Pelorus Sound.	137

## Executive summary

In July 2011 Marlborough District Council (MDC) initiated a regular water-quality monitoring program for Queen Charlotte Sound and Tory Channel (five stations in total). From July 2012, this was extended to include Pelorus Sound (a further seven stations). From July 2013-April 2014, New Zealand King Salmon Ltd (NZKS) sampled water quality at several stations in Port Gore – one of these was at the Cook Strait mouth of the bay. After NZKS ceased sampling in Cook Strait, MDC sampled this outer-most Port Gore station in May and June 2014. Thereafter, NIWA has continued to sample at that site on a monthly basis (July 2014-June 2015). The three organizations have agreed to pool their data from this site for the purposes of this report. Since the NZKS, MDC and NIWA data all stem from the same location, we treat the collective data as a single data-set.

The MDC and NIWA water-quality data comprise monthly near-surface and near-bed measurements of nutrients (dissolved reactive silicon (DRSi), dissolved reactive phosphorus (DRP), nitrate ( $\text{NO}_3\text{-N}$ ), ammonical nitrogen ( $\text{NH}_4\text{-N}$ ), dissolved organic nitrogen, dissolved organic carbon, particulate carbon and nitrogen, chlorophyll, algal and zooplankton abundance (by cell counts) and biomass, volatile suspended solids (VSS) and total suspended solids (TSS). Water temperature, salinity, dissolved oxygen and Secchi disk depth are also measured. The NZKS data comprise a similar (but less extensive) suite of measurements.

Marlborough District Council commissioned NIWA to collate and summarize the resultant water-quality data in this report. Detailed commentary and trend analysis/cross-correlation analyses etc., were not required. Data are shown as station-specific time-series and the probability distributions of measurement values are also illustrated with a view to enabling Council staff to develop 'quality control flag values' that will make it easier to identify outlier data in the future. The report describes instances (and reasons) where data have been rejected and offers commentary upon possible changes to the sampling program and ways in which the data may influence management of the Sounds.

## 1 Introduction

In July 2011 Marlborough District Council (MDC) initiated a regular water-quality monitoring program for Queen Charlotte Sound and Tory Channel. From July 2012, this was extended to include Pelorus Sound. Marlborough District Council also sampled water-quality at the Cook Strait entrance of Port Gore for two months (May – June) in 2014. This sampling continued on a monthly basis from July 2014 to the present – but NIWA’s Government CORE-funded *Aquaculture Environment Interactions* programme covered the costs associated with the laboratory analyses of the water quality samples. New Zealand King Salmon Ltd. also sampled water-quality at several stations within Port Gore (incl. this one at the Cook Strait mouth) on a monthly basis from July 2013 to April 2014. They have made their data for the Port Gore (Cook Strait mouth) station available to us to be summarized within this report. Since the NZKS, MDC and NIWA data all stem from the same location, we treat the collective data as a single data-set.

Whilst parts of the collective data from Queen Charlotte/Tory and Pelorus have been shown as incidental material in earlier reports (Broekhuizen 2013; Hadfield, Broekhuizen et al. 2014; Broekhuizen, Hadfield et al. 2015), this is the first that is dedicated to presenting the data themselves and the first to present the Marlborough District Council/NIWA Port Gore data. This report does not offer any formal statistical analyses of trends, cross-correlations etc., in the data.

“Water-quality” is a term that has no unique or formal definition. The individual characteristics which contribute to water-quality can often be considered as falling into one (or both) of two categories: (a) those relating to the suitability of the water for direct human use (presence/absence of pathogens and toxins that might be harmful to humans (or marine species exploited- or otherwise valued- by humans), (b) those relating to aspects of ‘ecosystem health’. The latter category can include concentrations of suspended solids, nutrients, oxygen and plankton. It is important to realise that all of these materials are present even in pristine/unimpacted waters. Furthermore, the ‘natural’ abundance of any one characteristic may vary across differing ‘pristine’ systems. A concentration that might be deemed to be unusually high (or low) in one (modified/stressed) system might be entirely natural for some pristine systems.

A water-body may have low turbidity and colour but high concentrations of faecal contaminants. Those whose interest is in ‘sea-scape’ might consider the water-quality to be high, but those interested in contact recreation or shellfish farming are likely to consider the water quality to be low. Conversely, turbid water that is free of pathogens and toxins may remain safe for shellfish farming and swimming. Statements about water-quality are usually made with respect to an accompanying purpose/value: *this water is suitable for contact recreation, or these waters are not nutrient-enriched, so is unlikely to exhibit excessively large/frequent algal blooms or other unwanted symptoms of eutrophication.*

The MDC water-quality monitoring program was designed to monitor the trophic status of the Sounds. Thus, whilst water-quality characteristics such as clarity and concentrations of suspended solids, nutrients, oxygen and plankton are measured, there are no measurements of faecal contaminants, heavy metals or organic contaminants. Whilst the data were gathered with a view to monitoring trophic status, we have been asked only to present the monitoring data. We make no formal assessment of trophic status.

## 1.1 Water Quality Standards (for trophic status)

A full review of water quality standard for coastal waters is beyond the scope of this report. Nonetheless, we offer a few relevant examples to provide some context that will help the readers to interpret the MDC Marlborough Sounds water-quality monitoring data.

Other relevant sources include: (Paerl 1997; Vollenweider, Giovanardi et al. 1998; Smith, Tilman et al. 1999; Rabalais 2002; Smith 2006; Rabalais, Turner et al. 2009; Sutula 2011; Hartstein and Oldman (in prep)).

**Table 1-1: Examples of coastal water-quality thresholds and/or standards relevant to the Marlborough Sounds.** Note that where standards are attributed to Morrisey, Anderson et al. (2015), that document (rather than this table) provides the definitive description of the standard.

Property	Threshold(s)	Description of threshold(s)/band(s)	Comments	Reference
Ammoniacal nitrogen concentration	460 $\mu\text{g L}^{-1}$ total $\text{NH}_3\text{-N}$	Updated ANZECC marine guideline value (low risk of chronic or acute effects for human health)	At pH=8.0, and 20 °C	Batley,Simpson (2009)
Total nitrogen (dissolved and particulate)	300 mg N $\text{m}^{-3}$ in near surface waters	Threshold concentration in NZKS farm-management protocols (recent agreement between NZKS & MDC)	Three sequential near-surface TN concentrations > 300 mg N $\text{m}^{-3}$ (in monthly monitoring and beyond 250 m from farm perimeter) will trigger an investigation as to the cause. If the farms are deemed to be the cause an intervention may be required to reduce TN concentrations.	Morrisey, Anderson et al. (2015)
Chlorophyll concentration (seemingly, based upon highest values recorded during the 'annual bloom period' in near surface water)	5 $\mu\text{g chl L}^{-1}$	Consent condition for three recently approved NZKS salmon farms in the Marlborough Sounds		EPA Board of Inquiry consent conditions for new NZKS fish farms.
Chlorophyll concentration	3.5 $\mu\text{g chl L}^{-1}$	Threshold concentration in NZKS farm-management protocols (recent agreement between NZKS & MDC)	Three sequential chlorophyll exceedances (in monthly monitoring) will trigger an investigation as to the cause (farm or other) and, if the farms are deemed to be the cause an intervention may be required to reduce phytoplankton concentrations.	Morrisey, Anderson et al. (2015)
Dissolved oxygen concentration	4.4 mg $\text{L}^{-1}$	Median concentration for sub-lethal effects in most sensitive taxonomic grouping examined (benthic fish)		Vaquer-Sunyer,Duarte (2008)

Property	Threshold(s)	Description of threshold(s)/band(s)	Comments	Reference
Dissolved oxygen concentration	70% throughout the water-column at locations <u>within</u> 250 m of farm perimeter	Threshold concentration in NZKS farm-management protocols (recent agreement between NZKS & MDC). Oxygen saturation should not drop below 70% at all sampling depths (but may drop below 70% at some depths)	More than three sequential breaches (in monthly monitoring) will trigger an investigation as to the cause. If the farms are deemed to be the cause an intervention may be required to reduce phytoplankton concentrations.	Morrisey, Anderson et al. (2015)
Dissolved oxygen concentration	90% throughout the water-column at locations <u>beyond</u> 250 m of farm perimeter	Threshold concentration in NZKS farm-management protocols (recent agreement between NZKS & MDC). Oxygen saturation should not drop below 90% at all sampling depths (but may drop below 90% at some depths)	More than three sequential breaches (in monthly monitoring) will trigger an investigation as to the cause. If the farms are deemed to be the cause an intervention may be required to reduce phytoplankton concentrations.	Morrisey, Anderson et al. (2015)

## 2 The monitoring program

### 2.1 Monitoring locations & methods

MDC have sampled in Queen Charlotte Sound/Tory Channel on an approximately monthly basis since July 2011 and in Pelorus Sound since July 2012. Sampling at the Cook Strait mouth of Port Gore has taken place on a monthly basis since April 2014<sup>1</sup>.

There are eleven sampling stations in each of the two Sound systems (Figure 2-1). The Port Gore station represents a twelfth sampling location. Sampling usually occurs in the third week of the month. In general, Pelorus Sound is sampled on one day and Port Gore/Queen Charlotte/Tory on the subsequent one. Occasionally, adverse weather has delayed one or both sampling trips<sup>2</sup>. Thus, Queen Charlotte sampling has not always been one day after the corresponding Pelorus sampling. Similarly, in some years, there was no sampling in one given month, but two samplings in the subsequent one (early in the month, one late in the month).

In the Queen Charlotte/Tory and Pelorus data-sets, there are three distinct types of sampling:

1. A CTD (conductivity-temperature-depth) instrument is lowered through the water-column and then recovered. The instrument is equipped with sensors to measure PAR (photosynthetically active radiation), DO (dissolved oxygen) and fluorescence. Thus, this operation yields vertical profiles for temperature and salinity, dissolved oxygen, PAR (hence, light attenuation) and fluorescence (which tends to be dominated by fluorescence by phytoplankton pigments, but can also be influenced by dissolved colours (tannins etc.).
2. Secchi disk depth is measured (provides an index of water clarity). Secchi disk is a weighted white (sometimes black+white) disk that is lowered into the water on a string. The Secchi disk depth is the depth at which the person who is lowering the disk determines that they can no longer distinguish the disk.
3. Water samples are collected from close to the surface and close to the seabed. When recovered onto the boat, a sub-sample of the water is drawn and preserved with Lugols solution. The remainder of the sample is retained in a sealed bottle and packed in ice. The chilled and preserved samples are couriered to the NIWA water-quality laboratory in Hamilton over-night. The chlorophyll content of the water is determined on the day in which the samples arrive at the laboratory. The remaining raw water may then be frozen for several days until it becomes possible to conduct the remaining analyses (for nutrients, suspended solids etc.). Table 2-1 provides a summary of the water-quality properties that are measured and of the methods involved to make the measurements.

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<sup>1</sup> From July 2013-April 2014, New Zealand King Salmon Ltd. conducted water quality sampling at several sites (incl. this one) within Port Gore. Those earlier data are not presented within this report.

<sup>2</sup> In the case of Port Gore, sampling was not possible due to bad weather conditions and no replacement sampling was undertaken and thus there are missing data in the time-series).



CTD casts are made at all stations, but Secchi disk depth and water-sample collection occurs at only a subset of stations (four in Queen Charlotte, one in Tory, seven throughout Pelorus)<sup>3</sup>.

Near-bed water-samples are collected using a Van Dorn bottle that is lowered to approximately two meters above the seabed before being closed<sup>4</sup>. Up to (and including) June 2014, a Van Dorn bottle was also used to collect the near surface water sample (from about 1 m below the sea-surface), but from July 2014 onward, MDC switched to using a hose sampler. A weighted hose pipe is lowered to approximately 15 m depth. It is then sealed and recovered. The hose is drained into a bucket. The bucket is stirred and a sample is drawn from the bucket. Thus, the water-sample represents a depth-average over the upper 15 metres of the water column. At the two inner-most sites in Pelorus Sound (PLS-1 and PLS-2), the hose sampler would reach to the seabed if fully extended. Thus, for these two sites, it was decided to cease collecting near-bed samples using the Van Dorn sampler (i.e., since the later part of 2014, there has only been one water-quality sample per month collected at these two sites. This has been a depth-integrating hose-sample.

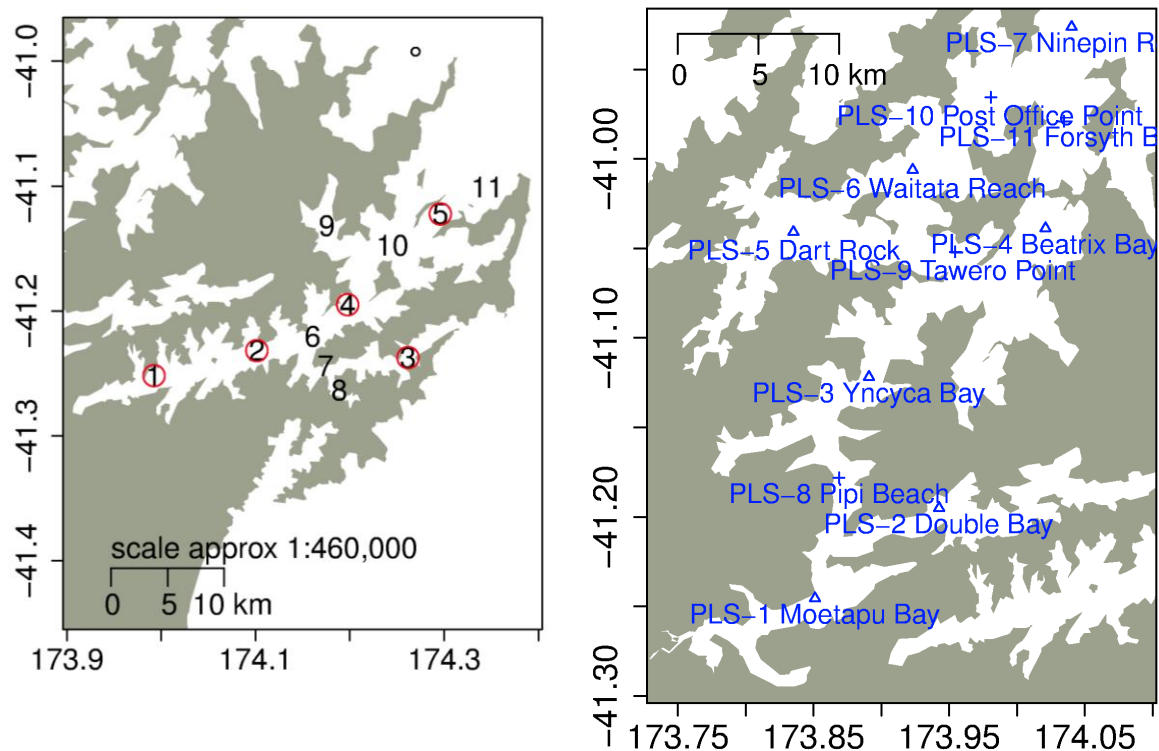
Prior to July 2014, water samples were analysed for particulate organic carbon (POC) and particulate organic nitrogen (PON). From July 2014 onward, these characteristics were dropped in favour of particulate carbon (PC) and particulate nitrogen (PN). The change was made to render the MDC sampling more consistent with other historical data gathered in Pelorus Sound. The laboratory methods for sampling PC and PN are slightly simpler than those for POC and PON (the former requires less filtration, so may be less prone to laboratory error). Historical data from Pelorus Sound indicate that PON and PN have near 1:1 relationship with one another. The POC and PC values are also correlated with a slope that is close to 1.0 (Broekhuizen 2014). We therefore regard the two suites of measures as being quantitatively equivalent. We concatenate the POC and PC time-series to a single, composite time-series (that we will call particulate organic carbon (POC)). Similarly, we concatenate the PON and PN data to yield a single composite time-series ('particulate organic nitrogen' (PON)).

The sampling regime at Port Gore has been conceptually similar to those of Queen Charlotte/Pelorus but, for historical reasons, the suite of water-quality quantities which are measured has been a little more restricted.

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<sup>3</sup> The hand-held temperature, salinity and dissolved oxygen sensors are owned and maintained by Marlborough District Council. Up until July 2014 (incl), the Council used a NIWA CTD (with DO sensor and fluorometer) to make the vertical casts. From August 2014, they used a CTD of their own. They take responsibility for maintaining the sensors on that CTD.

<sup>4</sup> On rare occasions, the bottle has hit the seabed before being closed. Such events can stir sediments up off the bed such that anomalously high suspended sediment concentrations are measured. When the laboratory records unusually high suspended sediment concentrations, we have contacted MDC staff to determine whether the bottle was recorded as having hit the seabed. When this is confirmed the data are rejected,



**Figure 2-1: Locations of the Marlborough District Council sampling stations.** (left) Queen Charlotte Sound/Tory Channel and Port Gore; (right) Pelorus Sound. For Queen Charlotte/Tory, circled numbers denote water-quality sampling stations and unadorned numbers denote CTD-only stations. The black circle indicates the Port Gore sampling station. For Pelorus, water-quality stations are denoted with a triangle whilst CTD-only stations are denoted with a cross.

**Table 2-1: Characteristics measured in each water-quality sample.**

Quantity	Abbreviation	Units	Laboratory Method	Detection limit	Comment
Salinity	Sal	ppt		0.1	
Turbidity	Turbidity	Nephelometric turbidity units (NTU)	Turbidimeter rated against Formazin standards (APHA2130B)	0.1	
Total suspended solids	TSS	g DW m <sup>-3</sup>	Filtration (GF-C), drying at 104 C (APHA 2540D)	0.5	

Quantity	Abbreviation	Units	Laboratory Method	Detection limit	Comment
Suspended inorganic solids	SIS	g DW m <sup>-3</sup>	Filtration (GF-C), drying at 104 °C, followed by furnacing at 400 °C	0.5	
Volatile Suspended solids	VSS	g AFDW m <sup>-3</sup>	TSS-SIS	0.5	
Dissolved reactive silicon	DRSi	mg Si m <sup>-3</sup>	Molybdosilicate / ascorbic acid reduction. APHA4500Si	1	
Dissolved reactive phosphorus	DRP	mg P m <sup>-3</sup>	Simultaneous Auto-analysis (Astoria)	1	
Total dissolved phosphorus	TDP	mg P m <sup>-3</sup>	Persulphate digest, molybdenum blue, FIA (Lachat)	1	
Dissolved organic phosphorus	DOP	mg P m <sup>-3</sup>	TDP-DRP	1	Derived from the TDP and DRP measurements. We present this in addition to the TDP and DRP measurements
Ammoniacal nitrogen	NH <sub>4</sub> N	mg N m <sup>-3</sup>	Simultaneous Auto-analysis (Astoria)	1	
Nitrate+Nitrite	NO <sub>3</sub> N	mg N m <sup>-3</sup>	Simultaneous Auto-analysis (Astoria)	1	
Total dissolved nitrogen	TDN	mg N m <sup>-3</sup>	Persulphate digest, auto cadmium reduction, FIA (Lachat)	10	

Quantity	Abbreviation	Units	Laboratory Method	Detection limit	Comment
Dissolved organic nitrogen	DON	mg N m <sup>-3</sup>	TDN-NH <sub>4</sub> N-NO <sub>3</sub> N	1 (if NH <sub>4</sub> N+NO <sub>3</sub> N>10)	Derived from the TDN, NO <sub>3</sub> N and NH <sub>4</sub> N measurements. We present this in addition to those measurements
Chlorophyll-a	Chl	mg Chl m <sup>-3</sup>	Filter onto GF-C filter (approx. 1.2 µm pore size); Acetone pigment extraction, spectrofluorometric measurement.	0.1	
Particulate organic carbon	POC	mg C m <sup>-3</sup>	Filtration onto GF-C, acidification, Catalytic combustion @900°C, sep, TCD, Elementar C/N analyser	0.1	Prior to July 2014
Particulate organic nitrogen	PON	mg N m <sup>-3</sup>	Filtration onto GF-C, acidification, Catalytic combustion @900°C, sep, TCD, Elementar C/N analyser	0.1	Prior to July 2014
Particulate carbon	PC	mg C m <sup>-3</sup>	Filtration onto GF-C, Catalytic combustion @900°C, sep, TCD, Elementar C/N analyser	0.1	From July 2014
Particulate nitrogen	PN	mg N m <sup>-3</sup>	Filtration on GF/C, Catalytic combustion @900°C, sep, TCD, Elementar C/N analyser	0.1	From July 2014
Taxon specific phytoplankton cell counts		Cell L <sup>-1</sup>		Variable, see appendix	Cell counts; also converted to carbon biomass

Quantity	Abbreviation	Units	Laboratory Method	Detection limit	Comment
Taxon specific zooplankton cell counts		Individuals L <sup>-1</sup>			Until June 2014

We will present the results from Queen Charlotte Sound / Tory Channel and Pelorus Sound in two separate sections. This reflects: (a) the differing durations of the time-series from each system, (b) the subtly different sampling dates for each system, (c) a convenient sub-division of the data into manageable chunks, (d) a natural geographic and hydrographic distinction [the influence of rivers upon flow and water-quality being of much greater import in Pelorus Sound].

## 2.2 CTD data

Different CTD instruments were used over the 4 year monitoring period.

From July 2011 to July 2013, a Seabird SBE19plus (serial number 4248) equipped with temperature, conductivity, PAR, fluorescence and turbidity was used with the exception of Sept 2011 when a Seabird SBE19plus (serial number 4337) with only temperature and conductivity sensors was deployed.

From August 2013 to March 2014, a YSI Sonde (serial number 13E101652) equipped with temperature, conductivity, fluorescence, BGA-PC fluorescence<sup>5</sup>, turbidity and dissolved oxygen sensors was used. The conductivity sensor on this instrument proved to be unreliable with the calibration appearing to drift over time. Conductivity and derived salinity and density appeared lower than expected with the error increasing over time. It has not been possible to satisfactorily correct the conductivity measurements in post-processing therefore all conductivity measurements over this period are rejected. Temperature data appear consistent with those measured with the Seabird (a comparison between this Sonde and Seabird 4248 was conducted in March and June 2014).

For April and May 2014, the Seabird SBE19plus (serial number 4248) was used for sampling, with a dissolved oxygen sensor added to the instrument.

June and July 2014 YSI Sonde serial number 14B100344 was used for sampling. However, the sensors from the original Sonde were moved over to this instrument, and again the conductivity data appear unreliable so have been rejected.

From August 2014 onwards, YSI Sonde serial number 14G100211 (owned by Marlborough District Council) has been used. This has the same array of sensors as described for the original Sonde except that the BGA-PC sensor is replaced with a BGA-PE sensor<sup>6</sup>. The data from this instrument appear to date to be consistent and reliable.

<sup>5</sup> Phycocyanin Blue-Green Algae Sensor (BGA-PC) measures blue-green algae pigment fluorescence. The sensor has not been calibrated to field samples of blue-green algae. Furthermore this sensor is designed for freshwater and estuarine conditions.

<sup>6</sup> Phycoerythrin Blue-Green Algae Sensor (BGA-PE). This is similar to the BGA-PC sensor but intended for marine and estuarine conditions.

CTD data were post-processed to remove the up-cast (only the down-cast is used, most CTD instruments are optimised to sample on the downcast) and the period that the instrument is held at the surface. Any obvious spikes etc., were removed (see also Table 6-1). Salinity and density were calculated from temperature and conductivity. Note that salinity is reported here as absolute salinity (ICOR, SCOR et al. 2010) which replaces practical salinity calculated by the YSI software<sup>7</sup>. Data were binned (averaged) into 1m increments.

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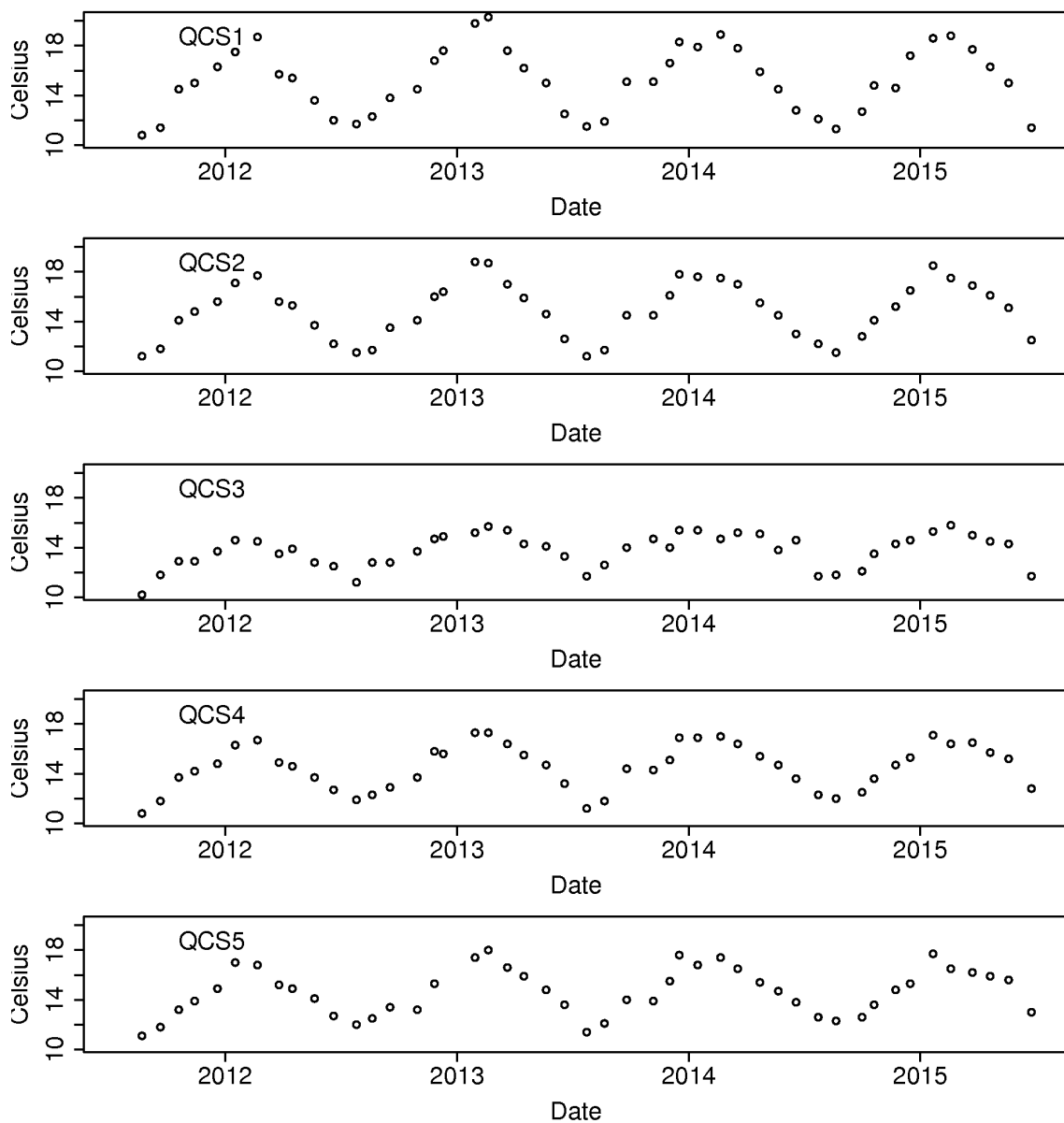
<sup>7</sup> Absolute salinity ( $S_a$ ) is defined as the mass fraction of dissolved solids within a kg of water ( $\text{g kg}^{-1}$ ). This mass fraction is difficult to measure on a routine basis. For that reason, the practical salinity scale ( $S$ ) has been widely adopted as a ready means making routine measurements measuring salinity. It is based upon a relationship between conductivity and salinity. Unfortunately, (i) conductivity is strongly influenced by temperature and, (ii) whilst non-ionic dissolved solids contribute to absolute salinity, they make no contribution to practical salinity. These factors limit the both the accuracy and the precision with which absolute salinity can be inferred from conductivity. Empirically,  $S_a=(1.0045 \pm 0.0005)S$

### 3 Results (Queen Charlotte Sound)

#### 3.1 Temperature

##### 3.1.1 Hand-held surface temperature

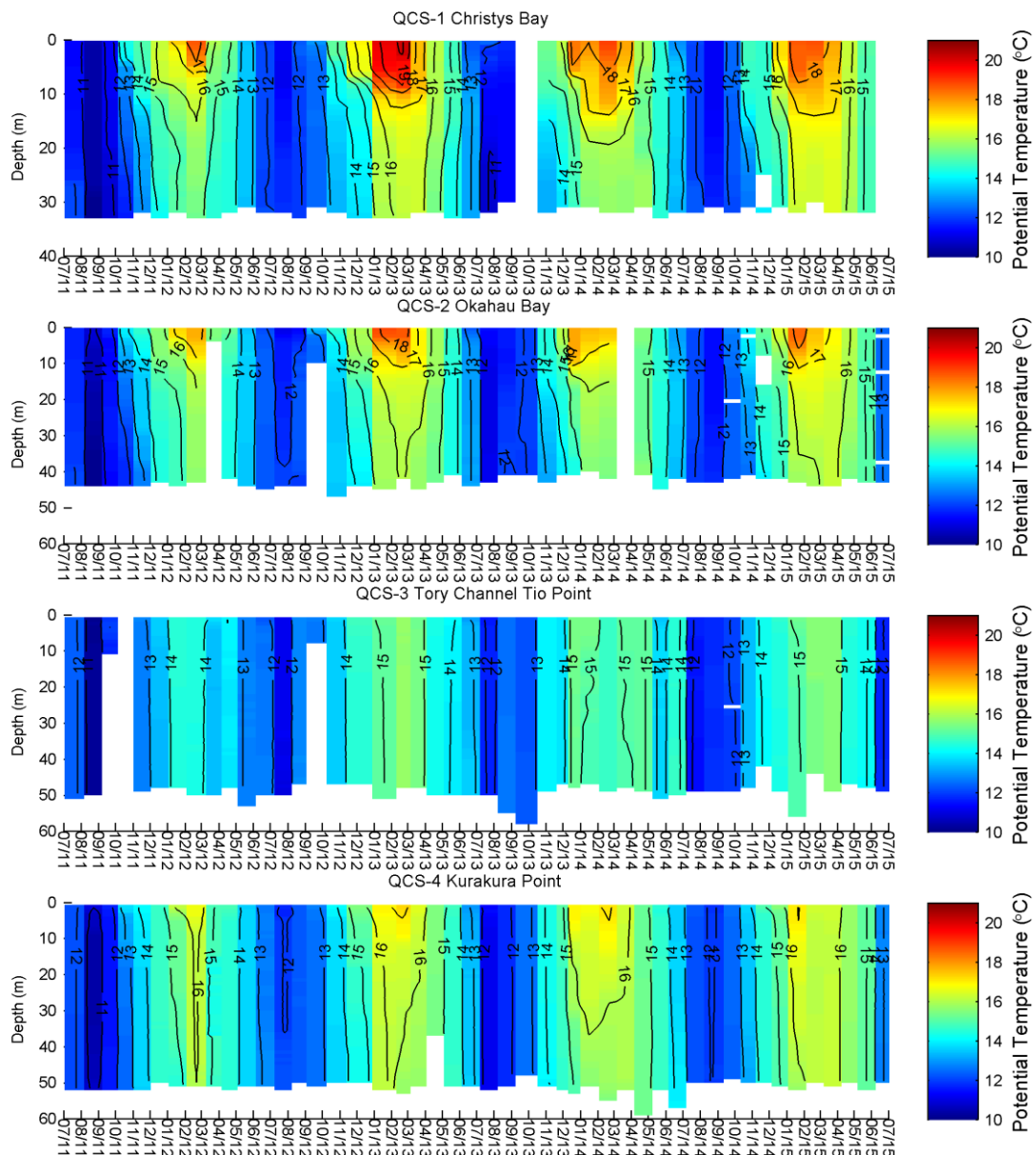
The phase of the annual temperature cycle is similar at all sites and in all years. The winter minimum occurs around August and the summer maximum around February. The winter minima are around 10-11 °C at all sites, but the summer maxima differ. The coldest summer-time surface water temperatures [14-15 °C] are found in Tory Channel (QCS-3). The warmest [approx. 18 °C] are found in Grove Arm (QCS-1, QCS-2).



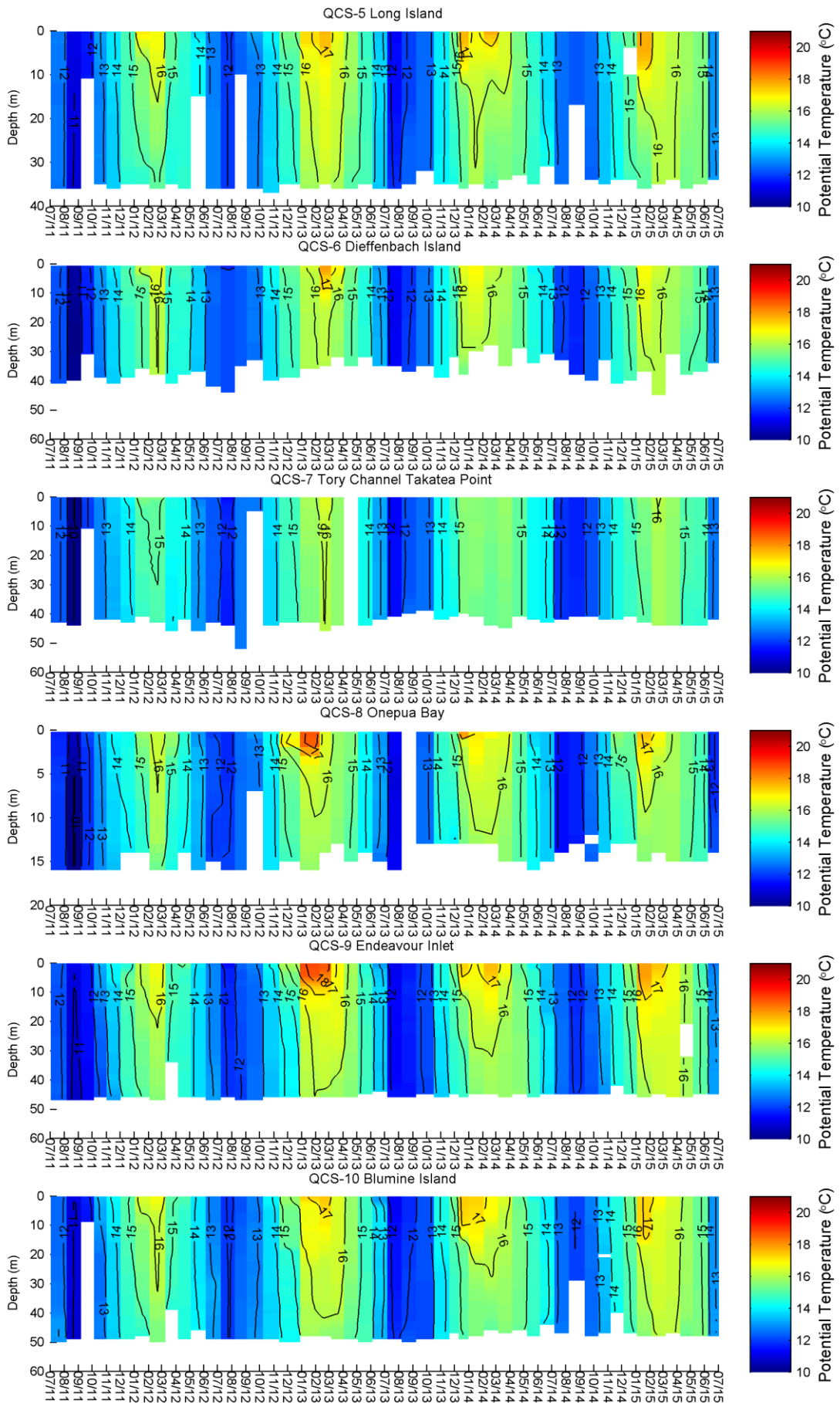
**Figure 3-1: Queen Charlotte: Near surface water temperature measured with a hand-held probe at each of the five water quality sampling stations.**

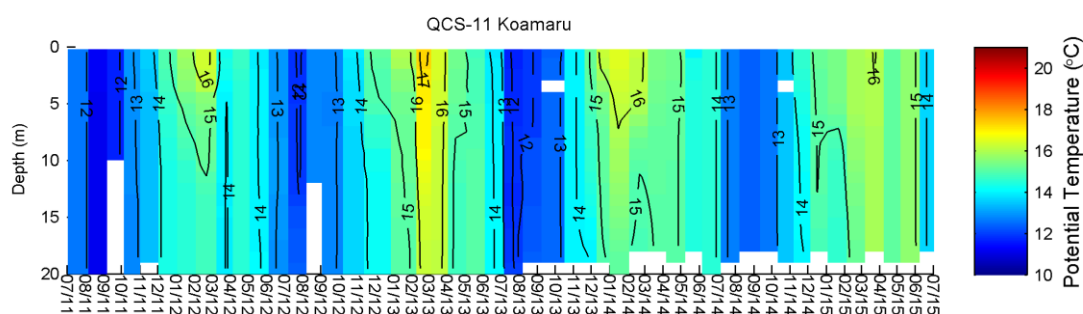
### 3.1.2 CTD temperature profiles

Depth-by-time contour plots of temperature show the season variations in temperature, and also the development of summer-time stratification in the inner sound (particularly sites QCS-1, 2) and side bays (QCS-8, 9) (Figure 3-2). Stratification starts to develop around November, and generally breaks up in April. Surface waters are warmest at the innermost site (QCS-1) with the highest temperature of 20°C recorded in late Feb 2013. Winter water temperatures drop to ~11-12°C throughout the sound. The Tory Channel (QCS-3, 7) remains relatively well-mixed year round.









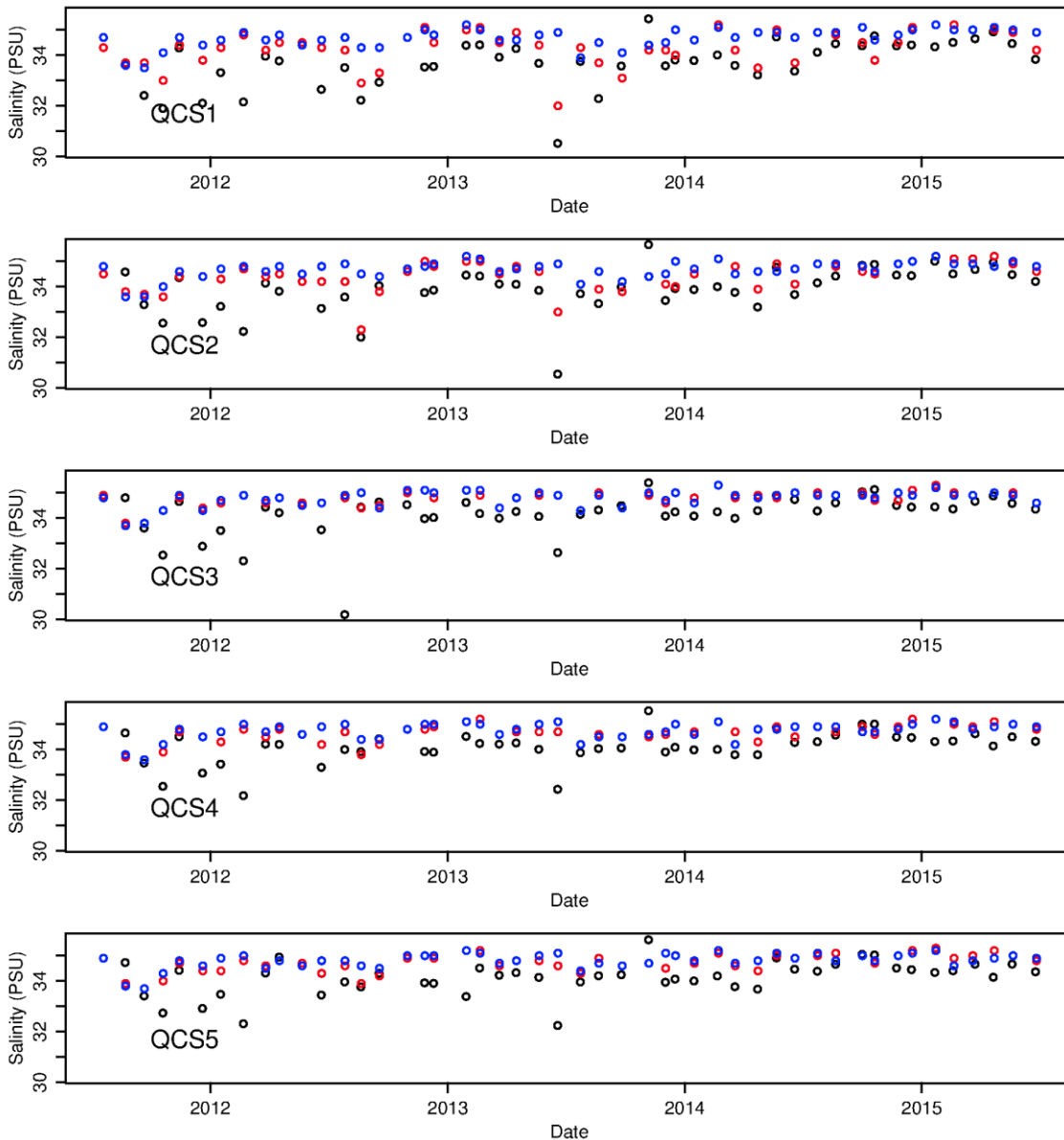
**Figure 3-2: Contour plots of the evolving depth profiles of temperature through time at the Queen Charlotte and Tory stations.** Data are from the monthly CTD casts. White space indicates missing/rejected data (or the maximum depth to which the cast extended).

## 3.2 Salinity

### 3.2.1 Hand-held surface salinity & laboratory determinations

As one might expect, near surface salinities tend to be a little lower than near-bed ones (Figure 3-1). Those measured in the laboratory tend to be a little higher than those measured at sea throughout the sampling period. This may indicate that the hand-held measurements and the Van Dorn bottle samples are made at slightly different depths, or it may indicate an inconsistency between the calibrations of the conductivity meters that are used in the field and in the lab. Near-surface salinities have invariably exceeded 30 PSU. Salinity minima tend to be lower within Grove Arm than in Tory Channel or central/outer Queen Charlotte. Whilst no formal cross-correlation tests have been made, salinities at different sites appear to be positively correlated – suggesting that the fluctuations at each site are all responding to one or more shared drivers (rainfall runoff, evaporation, intrusions from Cook Strait).

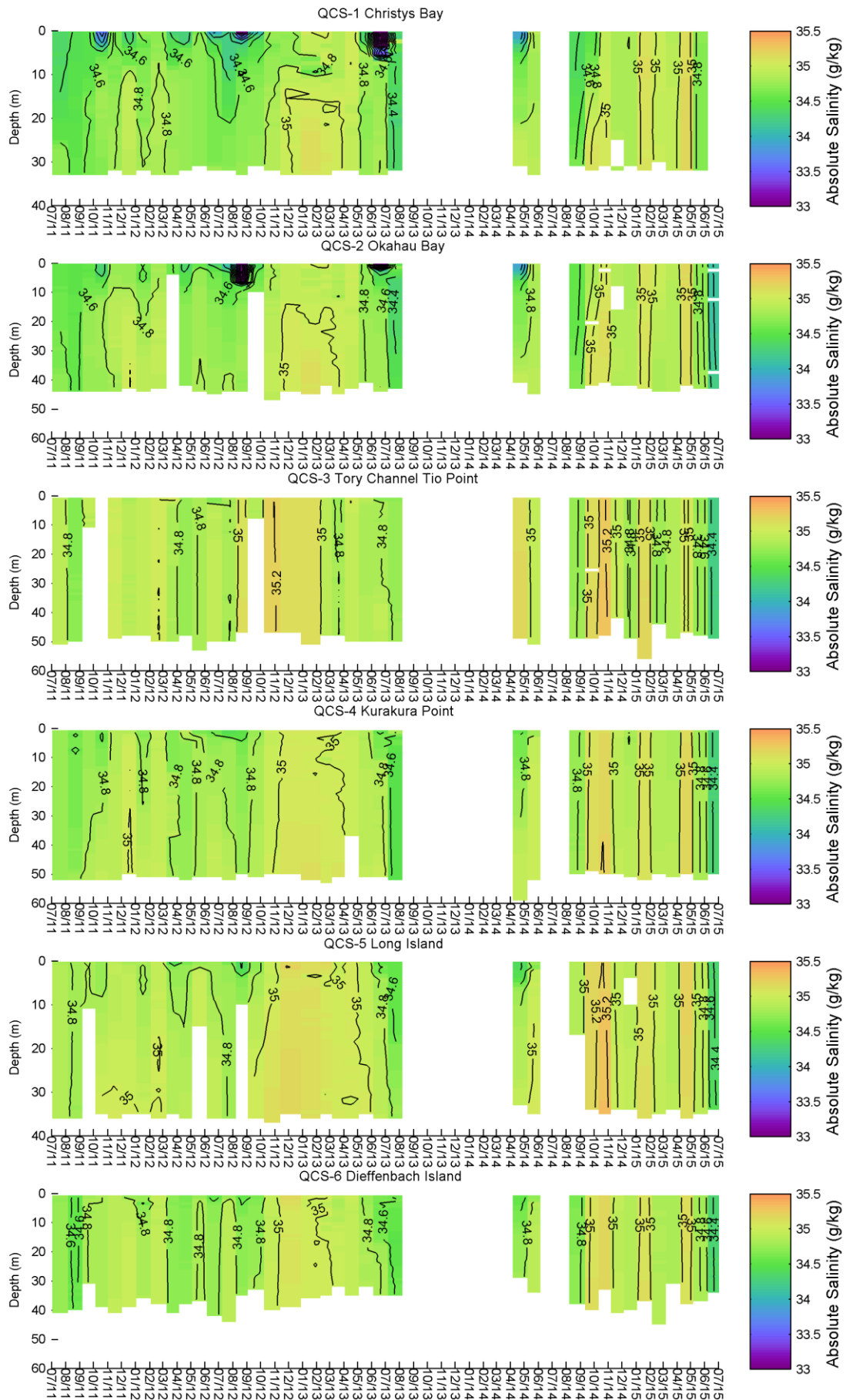
Looking at the at-sea near-surface salinity (black circles), one might conclude that there have been fewer (or less extreme) salinity minima since mid-July 2014 than prior to that date. This pattern is also evident (though much less so) in the laboratory salinity records. Were it evident only in the laboratory records, one might be tempted to conclude that it was driven by the switch from Van Dorn sampling (prior to July 2014) to depth-averaged (hose) sampling (to approx. 15 m deep) since then [fresh water is less dense than salty water, so samples drawn from one metre deep could legitimately be expected to have lower salinity than samples drawn from 0-15 m]. Since the pattern is (more) evident in the at-sea measurements (which have been made at one metre depth throughout the time-series), we infer that the absence of recent low-salinity events is, at least in part, a genuine feature. Presumably, either: (a) time-averaged rates of rainfall have been lower in the past 12 months or so than during some previous periods or (b) rainfall events have not immediately preceded sampling events during any of the past 12 months of sampling, but did so on some earlier occasions.

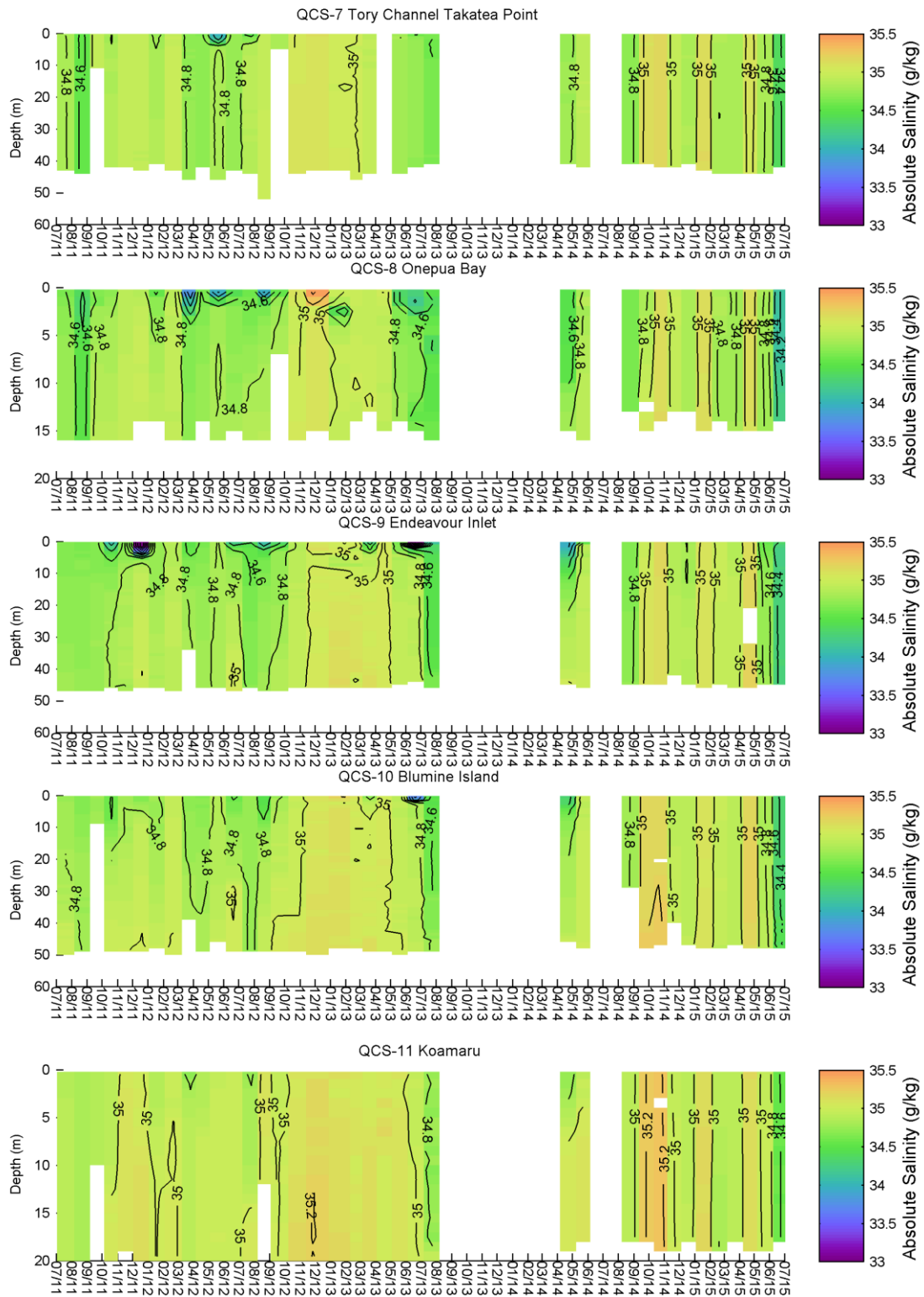


**Figure 3-3: Queen Charlotte: Salinity measured at sea with a hand-held probe at 1 m depth (black circles) and in water-samples returned to the laboratory (red circles: near surface (1m or depth averaged to 15 m); blue circles: near-bed). Different instruments were used to measure salinity at sea and in the laboratory.**

### 3.2.2 CTD salinity profiles

Contour plots illustrating the evolving depth profiles of salinity through time at the Queen Charlotte and Tory stations are shown in Figure 3-4. Variations in salinity are small between sites and over time. There are episodic low salinity events seen in surface waters, particularly at sites QCS-1, 2, 7, 8 and 9; and to a lesser extent at other sites. We assume that these were caused by rainfall and runoff. There is no obvious seasonal pattern. Note that large periods of salinity data from Sept 2013 to August 2014 are not shown due to calibration drift of the conductivity sensor.





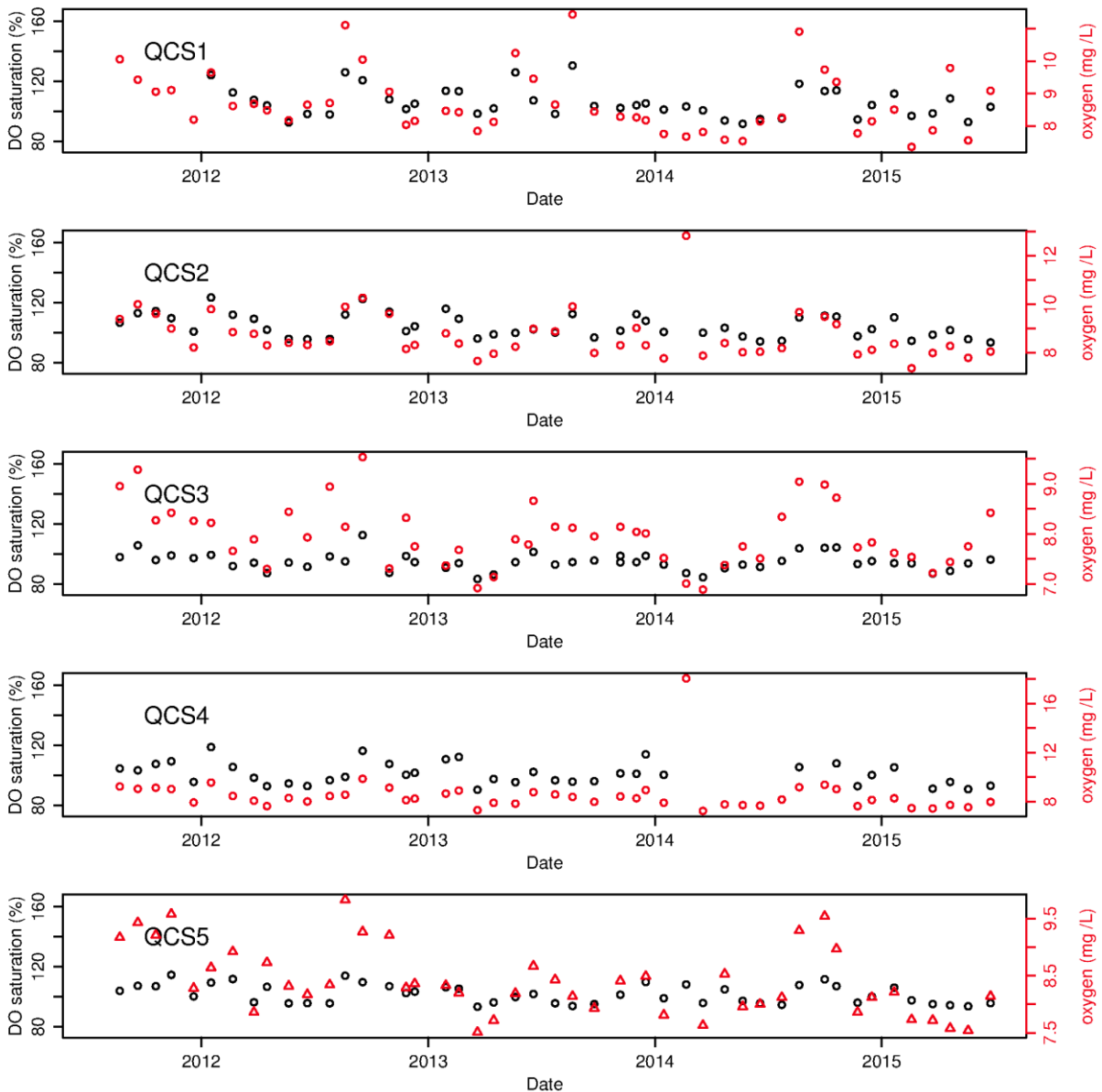
**Figure 3-4: Contour plots of the evolving depth profiles of salinity through time at the Queen Charlotte and Tory stations.** Data are from the monthly CTD casts. White space indicates missing/rejected data (or the maximum depth to which the cast extended).

## 3.3 Dissolved oxygen

### 3.3.1 Hand-held surface oxygen saturation

Near-surface dissolved oxygen concentrations have been high (>80% saturation) at all stations throughout the sampling period (Figure 3-5). Concentrations tend to be highest in spring and lowest in late summer/early autumn. Whilst some particularly sensitive species may begin to exhibit signs of mild stress as oxygen levels progressively further below about 80% saturation, in the literature, the median concentration for sub-lethal effects is about 4.2 mg O<sub>2</sub> L<sup>-1</sup> for even the most sensitive taxa (fish and crustacean) (Vaquer-Sunyer and Duarte 2008).

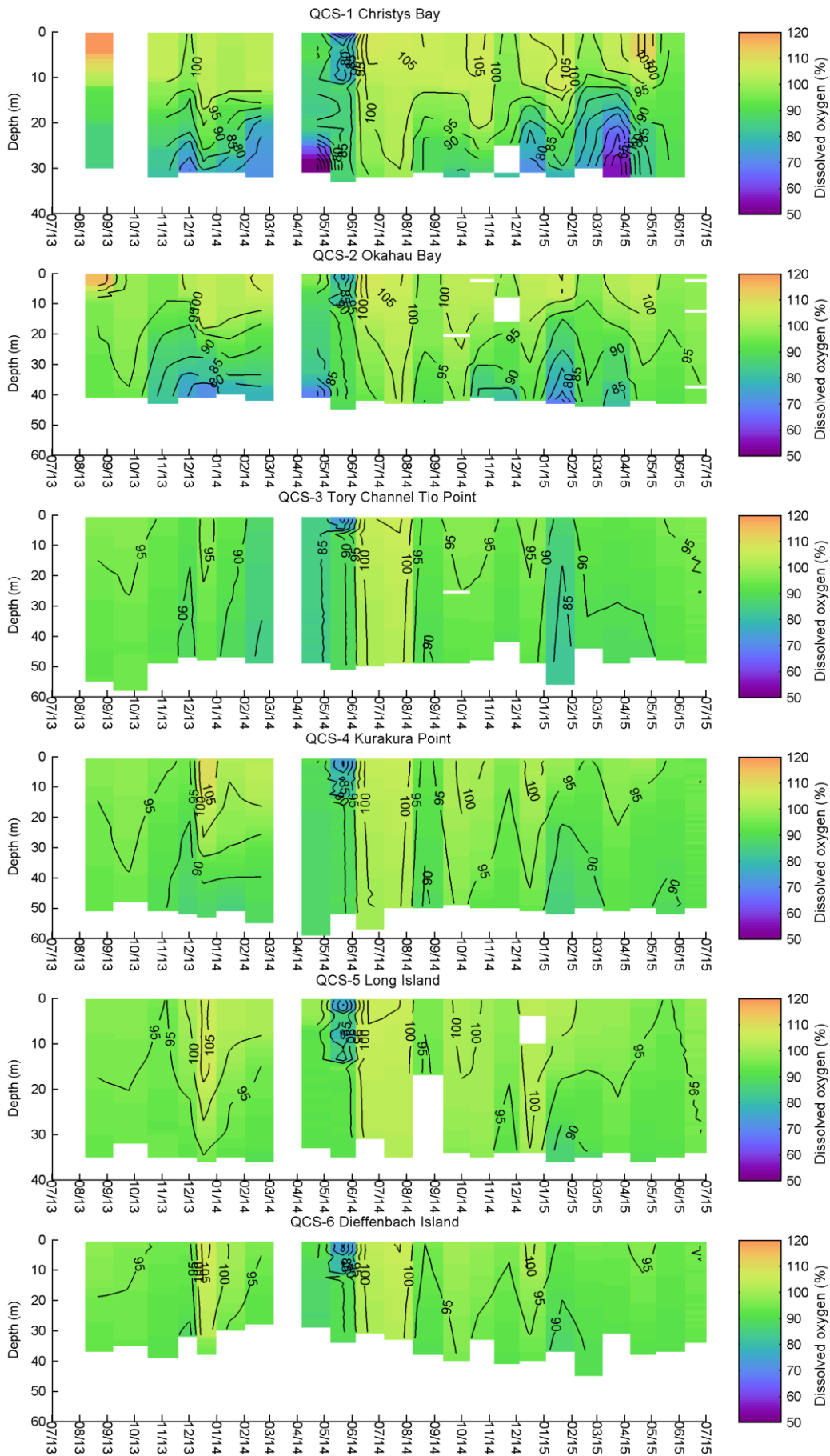
Near-surface concentrations of dissolved oxygen concentration have been high enough to sustain a healthy biota at every site on every sampling occasion. Near surface waters are in close contact with atmospheric oxygen. Furthermore, the surface waters receive plentiful light, so photosynthetic oxygen production can also be significant (for example, leading to mild oxygen super-saturation). In general, therefore one should expect that they will have high oxygen concentrations. In contrast, deeper waters are less well connected to the atmosphere and experience lower light intensities (lesser photosynthesis). Furthermore, nearbed waters must withstand both local (pelagic net oxygen demand) and net demand arising from the adjacent seabed. Thus, oxygen concentrations often tend to decline with increasing depth into the water-column. Information concerning the vertical distribution of oxygen is available from the DO sensors mounted on the CTD. These data are presented in 3.3.2.



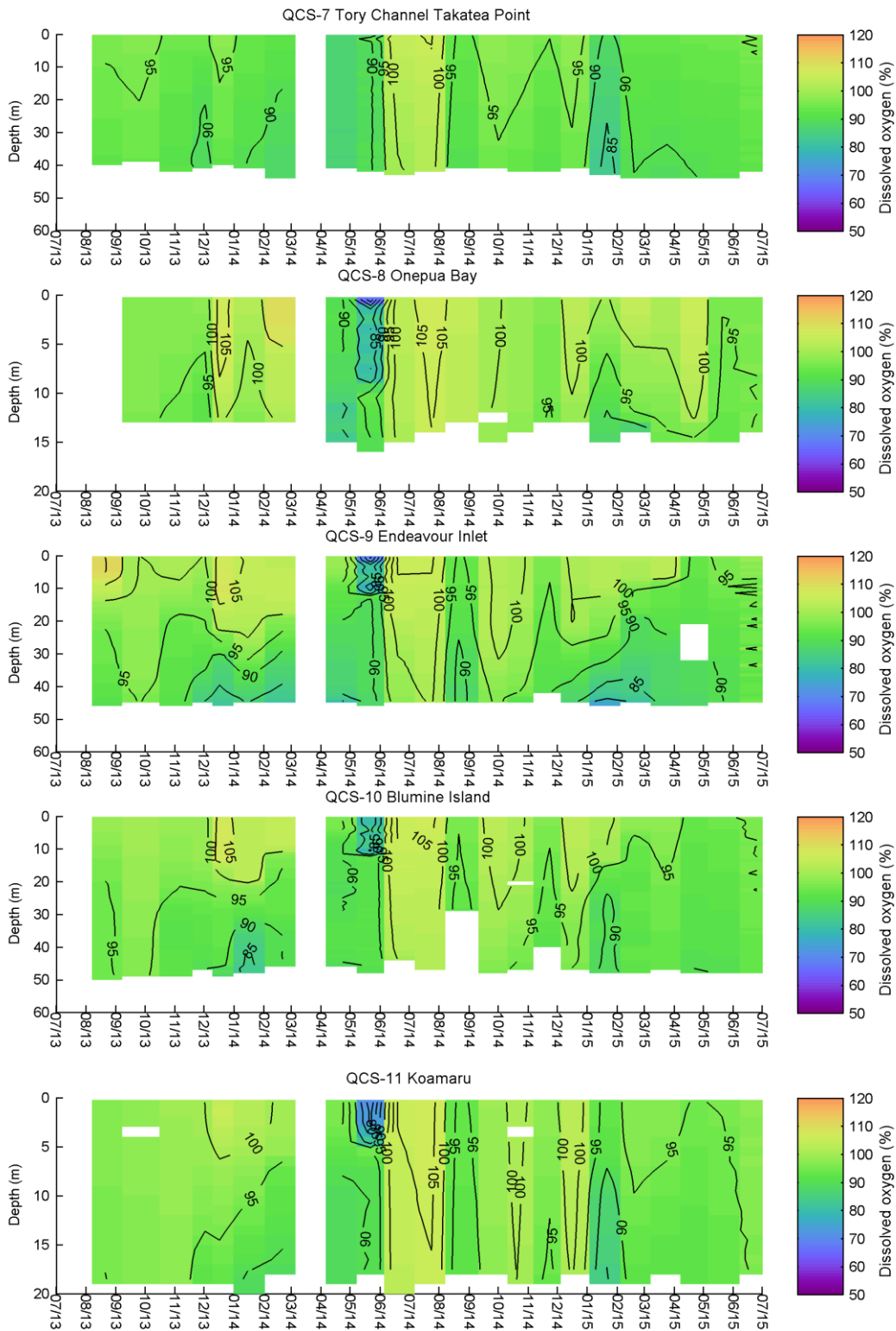
**Figure 3-5: Dissolved oxygen measured at one metre below the sea-surface at the five Queen Charlotte water-quality monitoring stations.** A small number of records from the hand-held sensor have been rejected as being implausibly high saturation (>140%) and concentration but others remain unresolved (see plots). Those records were replaced with near-surface readings from the CTD casts. Black symbols are oxygen saturation (left axis). Red symbols are concentration (right axis). Dissolved oxygen saturation is a function of salinity, temperature (and air pressure) as well as absolute oxygen concentration. Thus, the correlation with absolute oxygen concentration is strong, but imperfect.

### 3.3.2 CTD oxygen profiles

Contour plots of the evolving depth profiles of oxygen saturation through time at the Queen Charlotte and Tory stations from monthly CTD casts are shown in Figure 3-6.





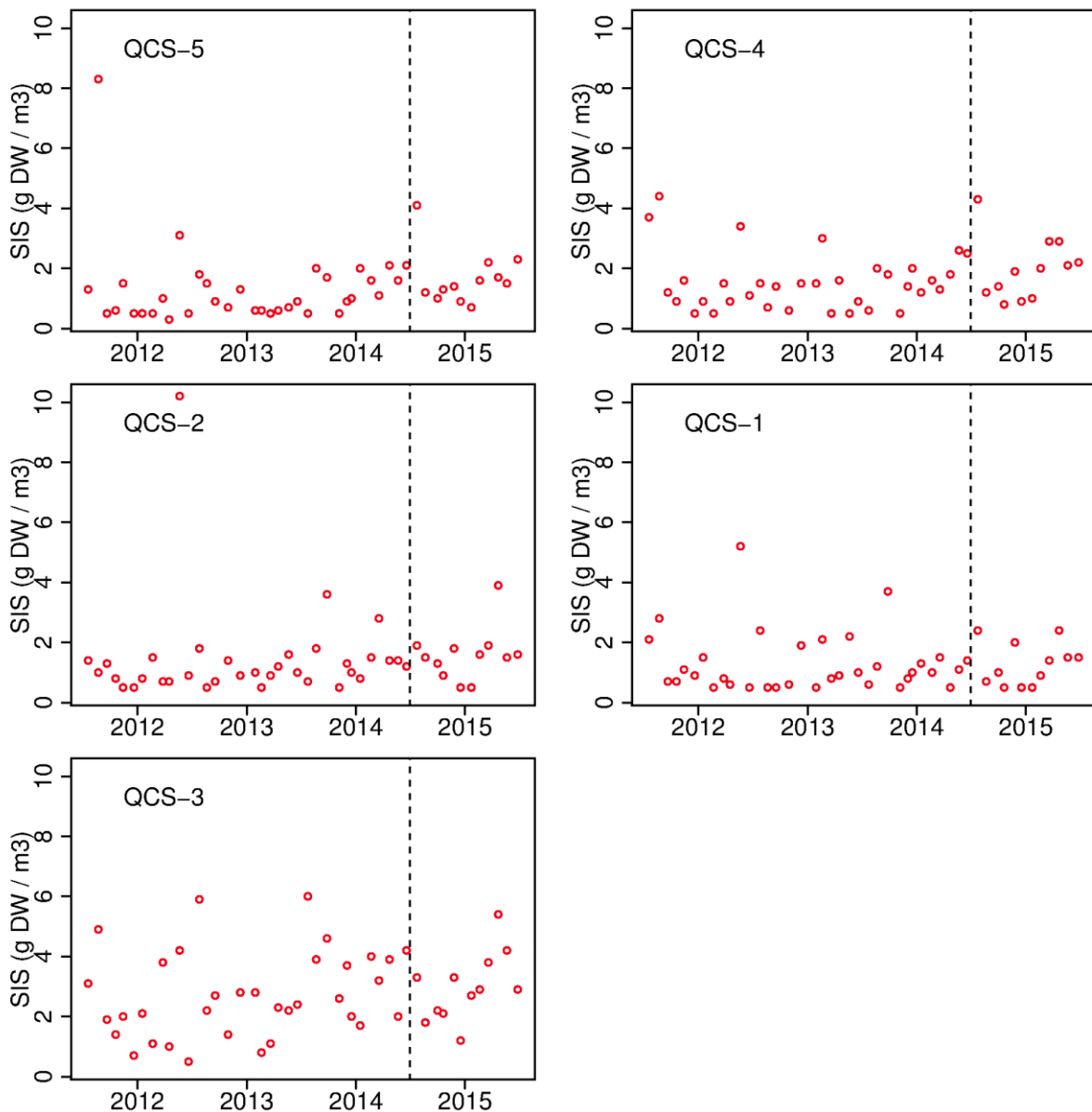


**Figure 3-6: Contour plots of the evolving depth profiles of oxygen saturation through time at the Queen Charlotte and Tory stations.** Data are from the monthly CTD casts. White space indicates missing/rejected data (or the maximum depth to which the cast extended).

### 3.4 Suspended inorganic solids

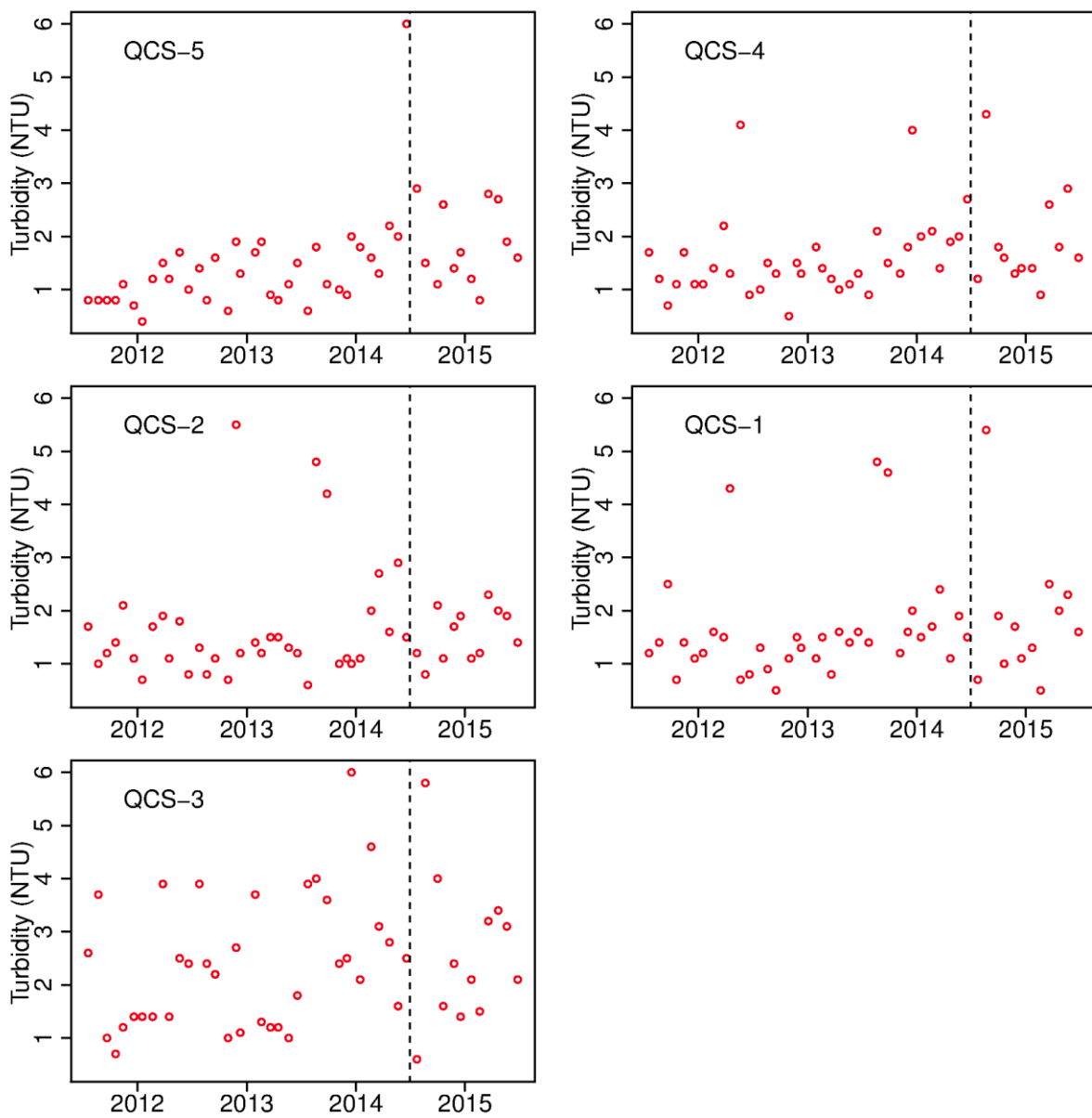
Concentrations of total suspended solids (TSS), suspended inorganic solids (SIS) and volatile suspended solids (VSS, equivalent to suspended organic matter) all derive from the same initial sample of material. The sample is first dried for several hours at 104 °C. This dry material is weighed to yield a TSS-weight. It then cooked at 400 C for several hours to burn off the organic material. The weight of the material that remains after cooking is the SIS-weight. The weight of volatile suspended solids is calculated as TSS-SIS.

SIS time-series for the 5 sites are plotted in Figure 3-7.



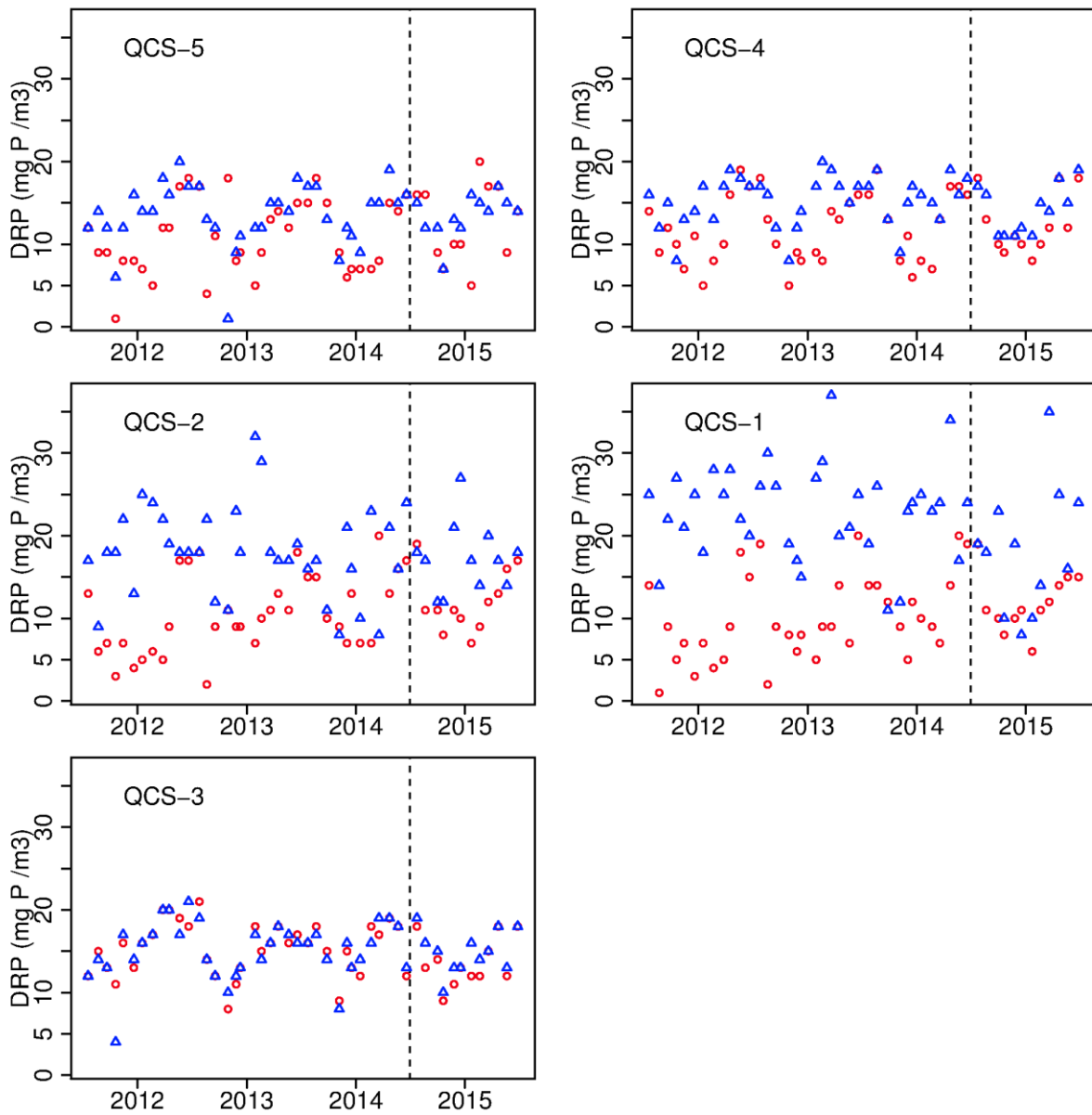
**Figure 3-7: Concentrations of suspended inorganic solids measured in the near-surface water-samples of the five Queen Charlotte Sound/Tory Channel stations.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

### 3.5 Turbidity



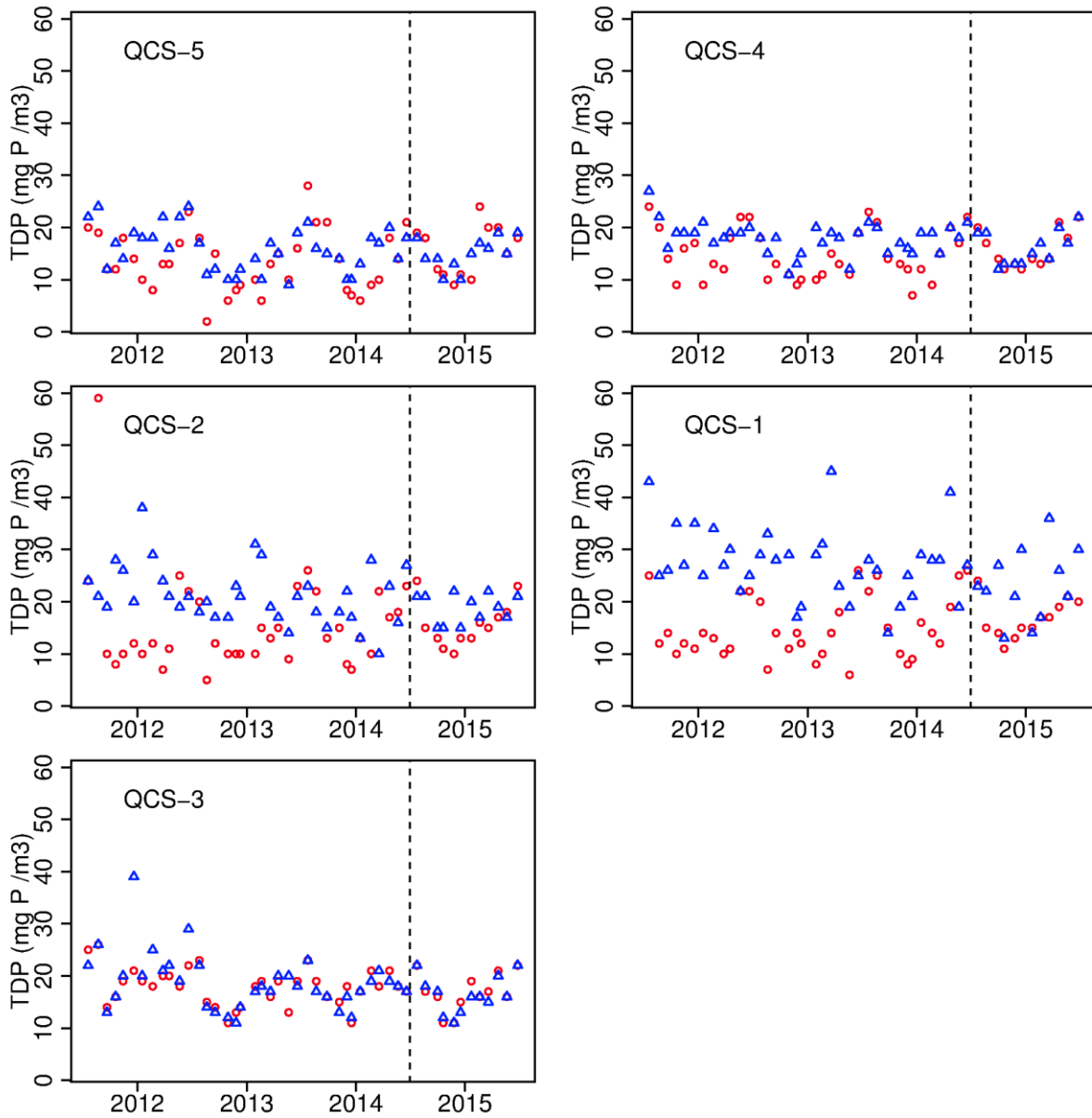
**Figure 3-8: Near-surface turbidity measured at the five Marlborough District Council water quality monitoring sites in Queen Charlotte/Tory Channel.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

### 3.6 Dissolved reactive phosphorus



**Figure 3-9: Time-series of dissolved reactive phosphorus measured near the surface (red) and near the seabed (blue) at the MDC sampling sites in Queen Charlotte Sound.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

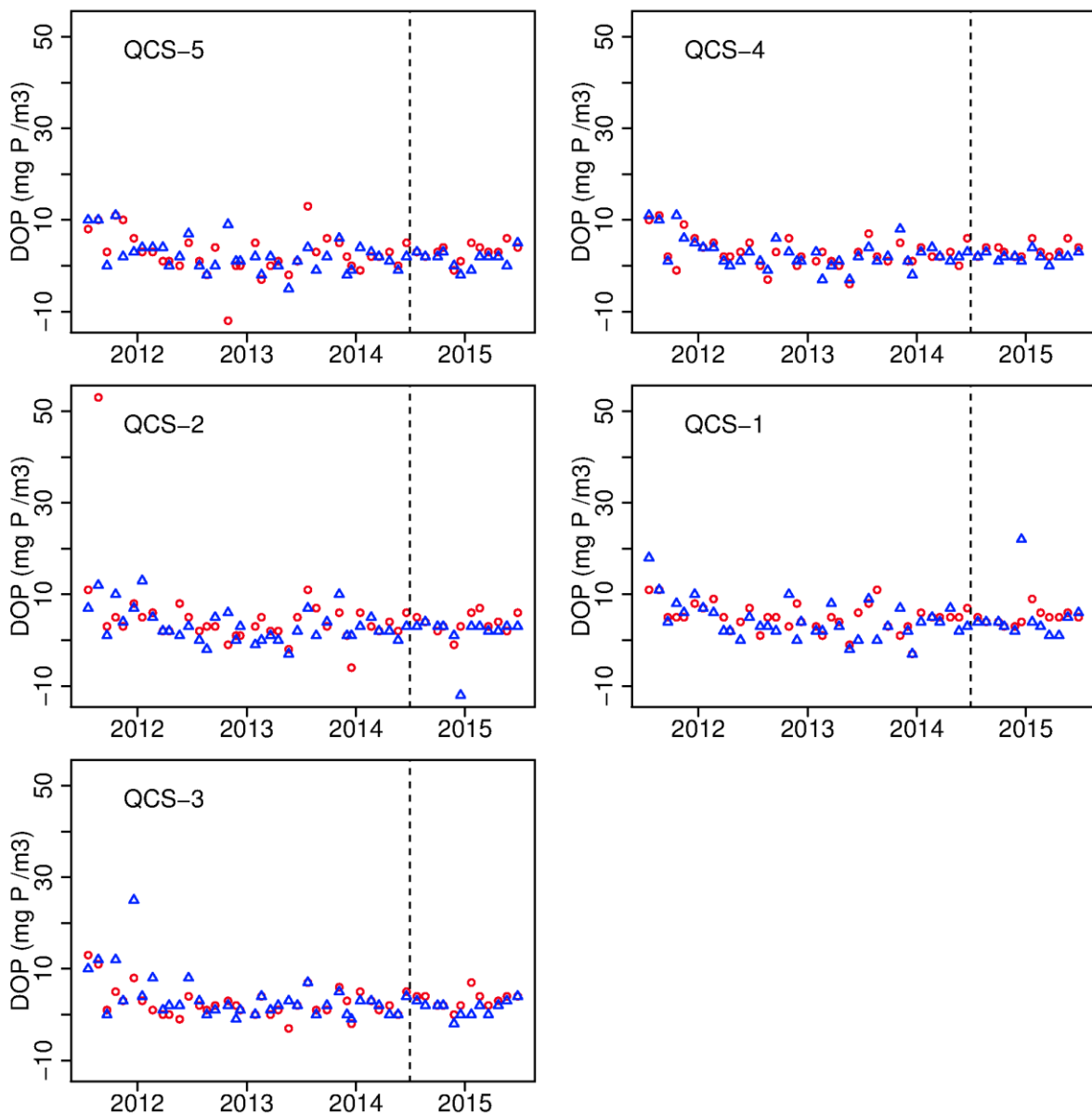
### 3.7 Total dissolved phosphorus



**Figure 3-10: Total dissolved near-surface (red) and near-bed (blue) phosphorus measured at the five Marlborough District Council stations in Queen Charlotte Sound.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

### 3.8 Dissolved organic phosphorus

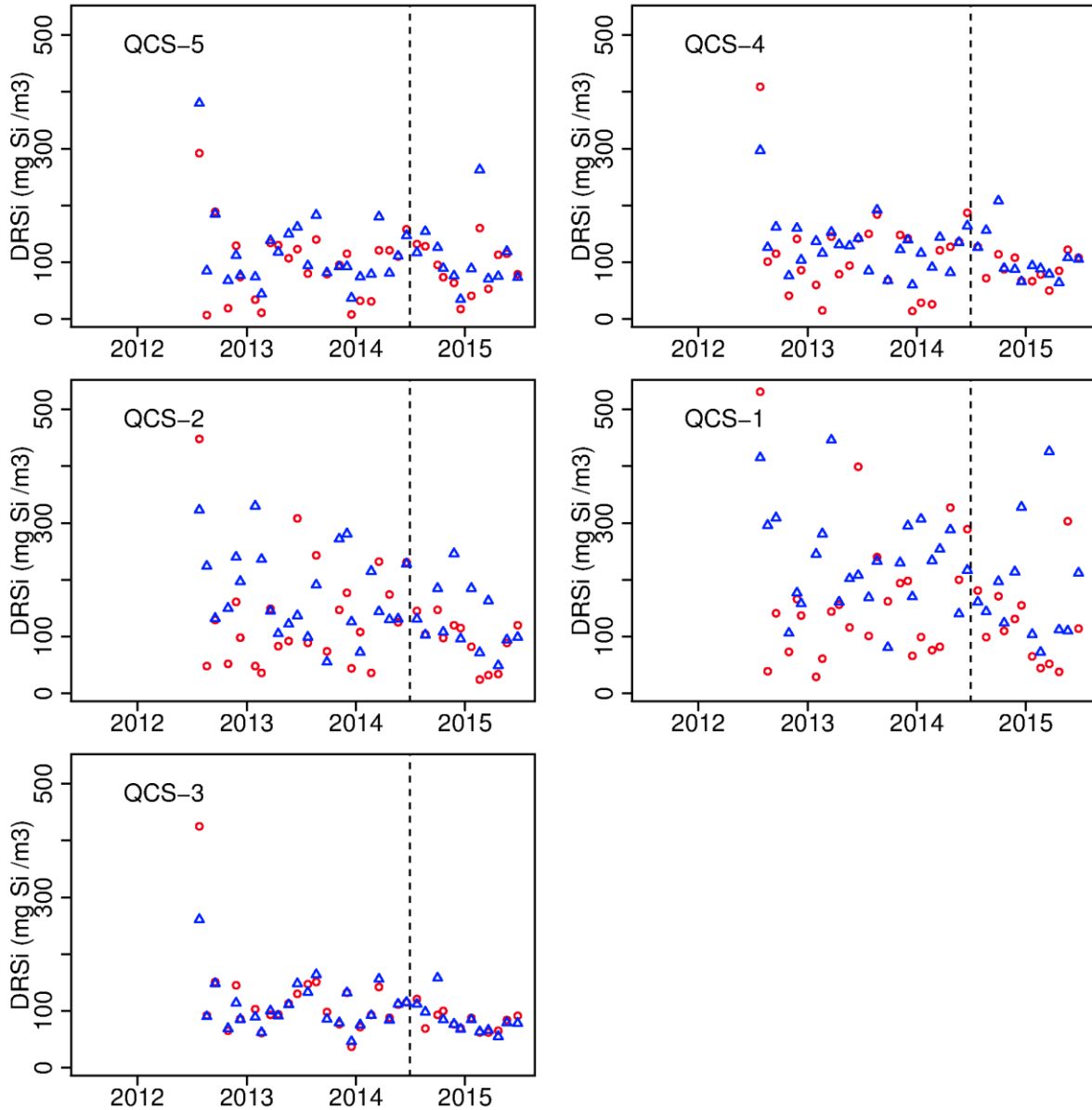
Dissolved organic phosphorus has been calculated by subtracting measured DRP concentrations from measured TDP concentrations. The inferred concentrations of dissolved organic phosphorus are usually low. Indeed, they are sometimes negative. In the real-world, negative concentrations are impossible. The negatives arise because of unavoidable sampling/measurement error (imprecision) associated with the measurements of DRP and TDP.



**Figure 3-11: Inferred near-surface (red) and near-bed (blue) dissolved organic phosphorus (TDP-DRP) at the five Marlborough District Council water quality sites in Queen Charlotte Sound. The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.**

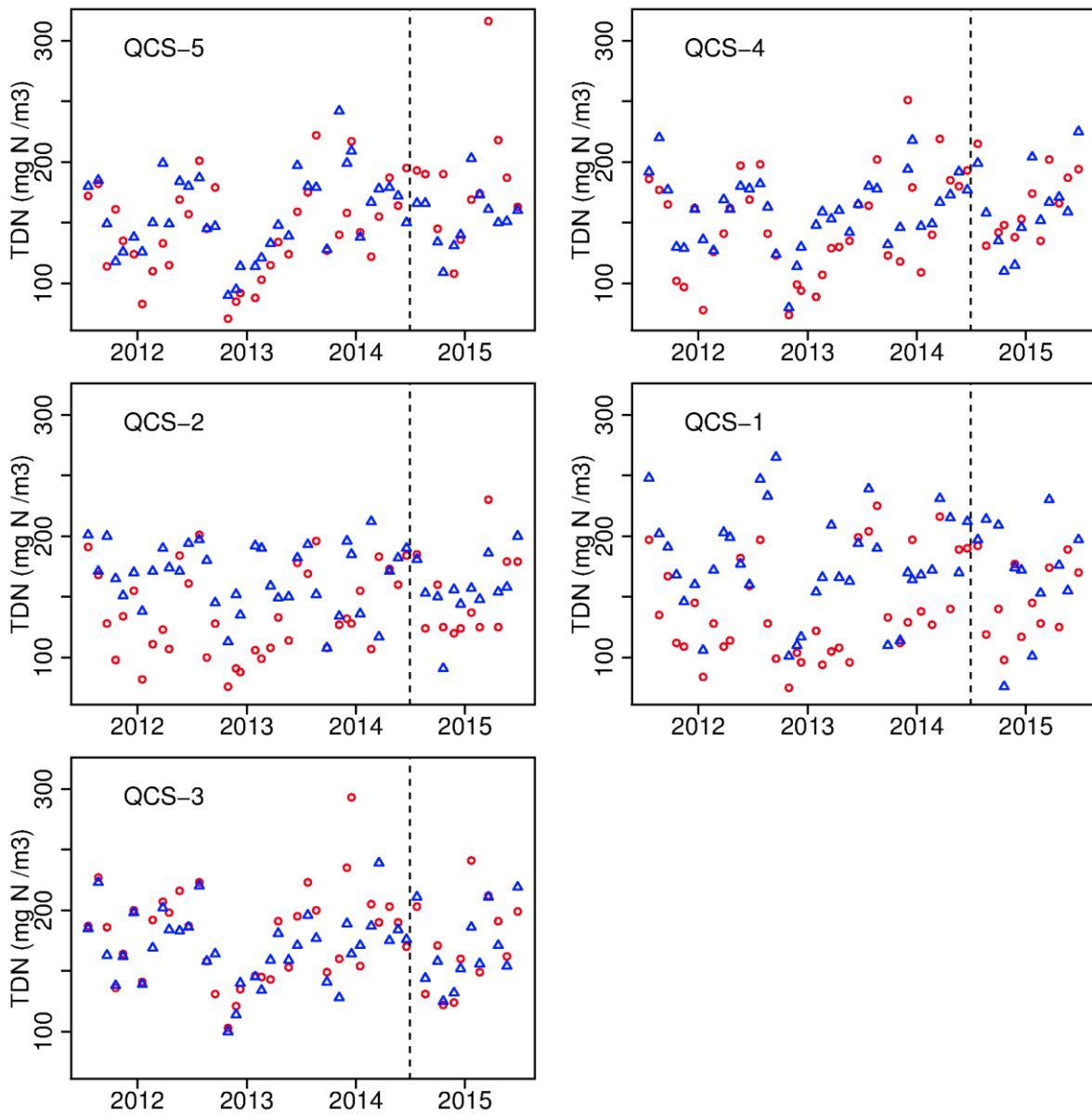
### 3.9 Dissolved reactive silicon

Dissolved reactive silicon was not measured during the first 12 months of the program.



**Figure 3-12: Dissolved reactive silicon concentrations near-surface (red) and near-bed (blue) at the five Marlborough District Council water quality stations in Queen Charlotte Sound.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

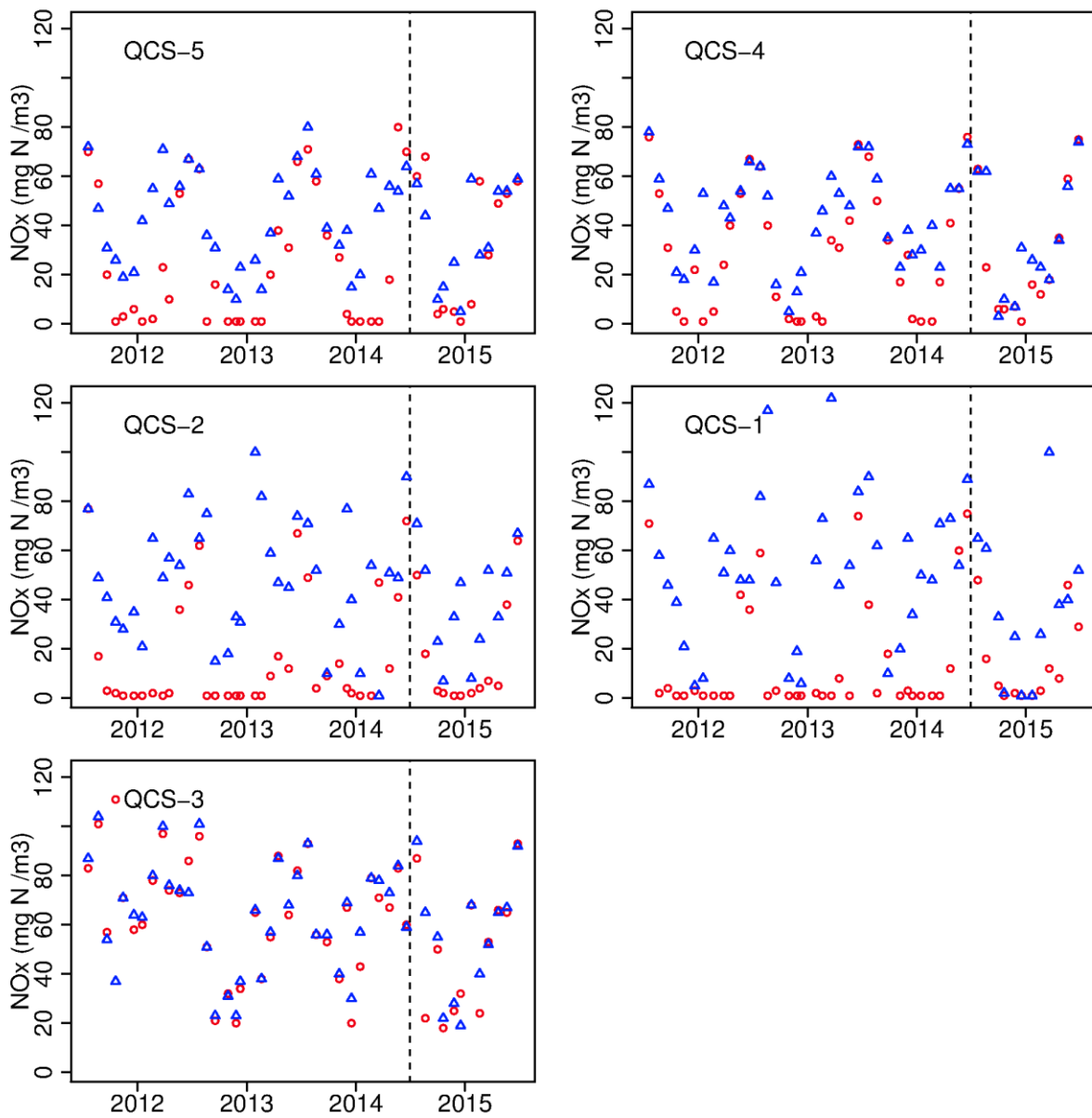
### 3.10 Total dissolved nitrogen



**Figure 3-13: Total dissolved nitrogen near-surface (red) and near-bed (blue) measured at the five Marlborough District Council water-quality stations in Queen Charlotte Sound.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

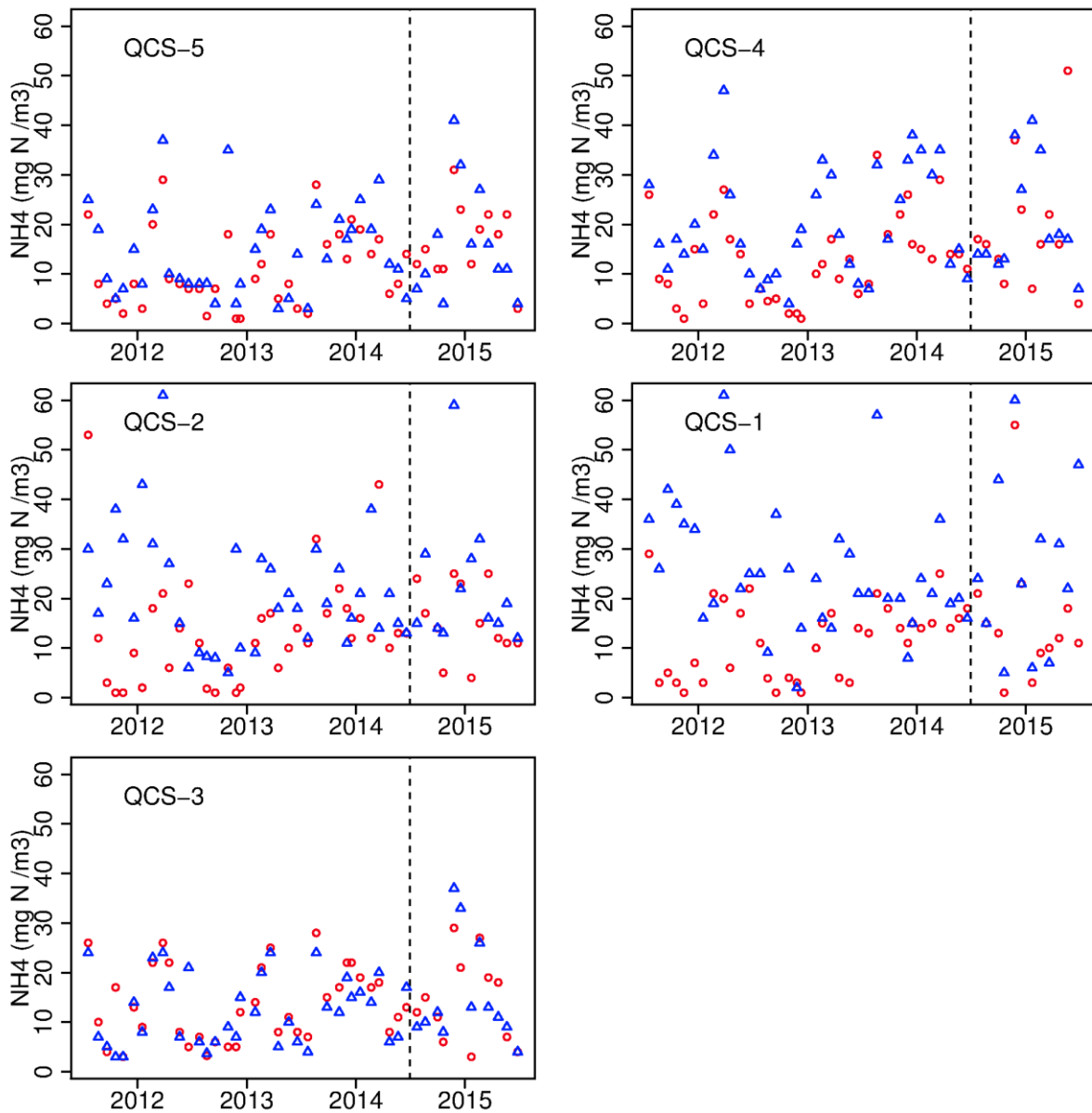


### 3.11 Nitrate



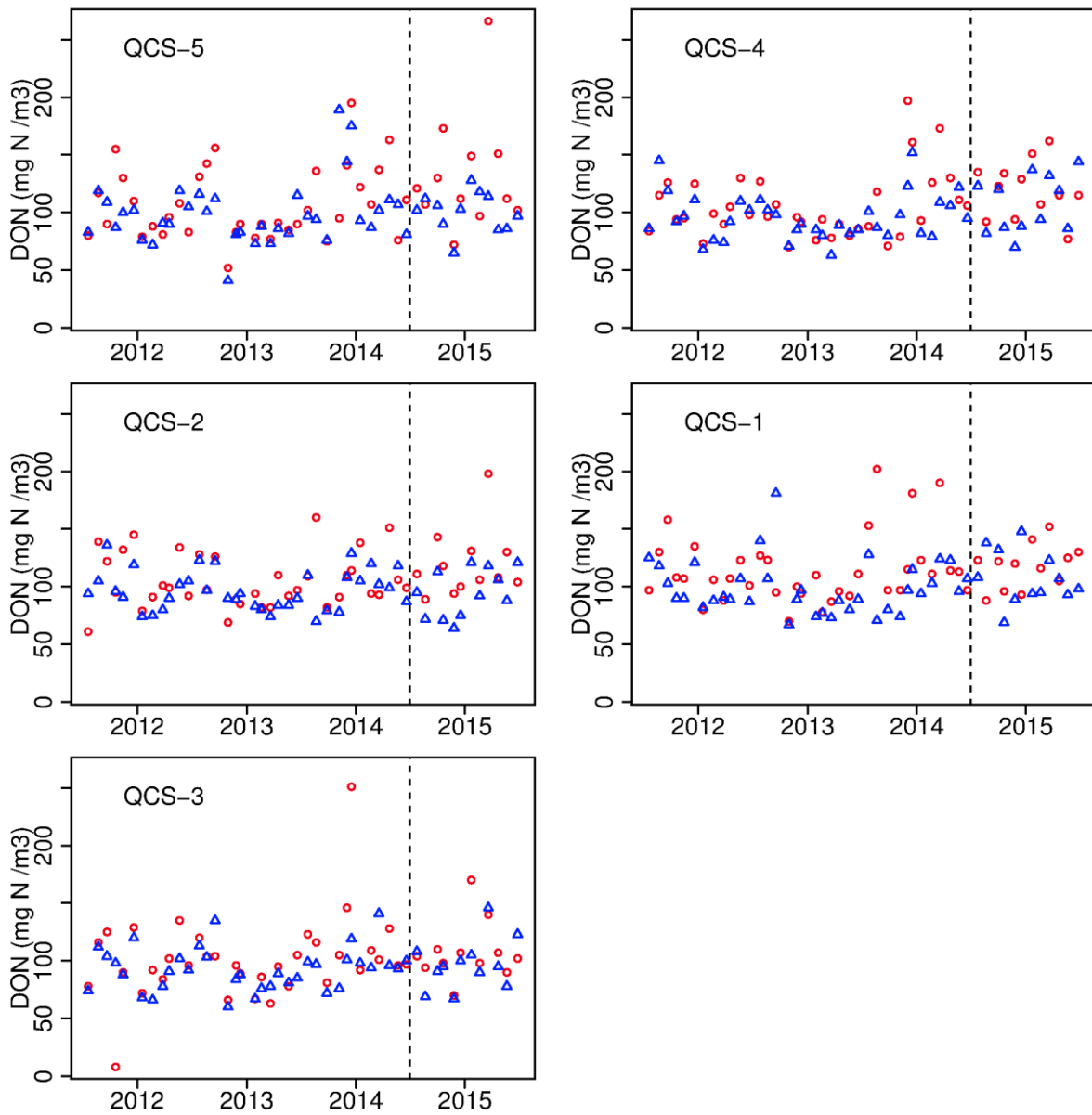
**Figure 3-14: Nitrate concentrations near-surface (red) and near-bed (blue) measured at the five Marlborough District Council water-quality stations in Queen Charlotte Sound.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

### 3.12 Ammoniacal nitrogen



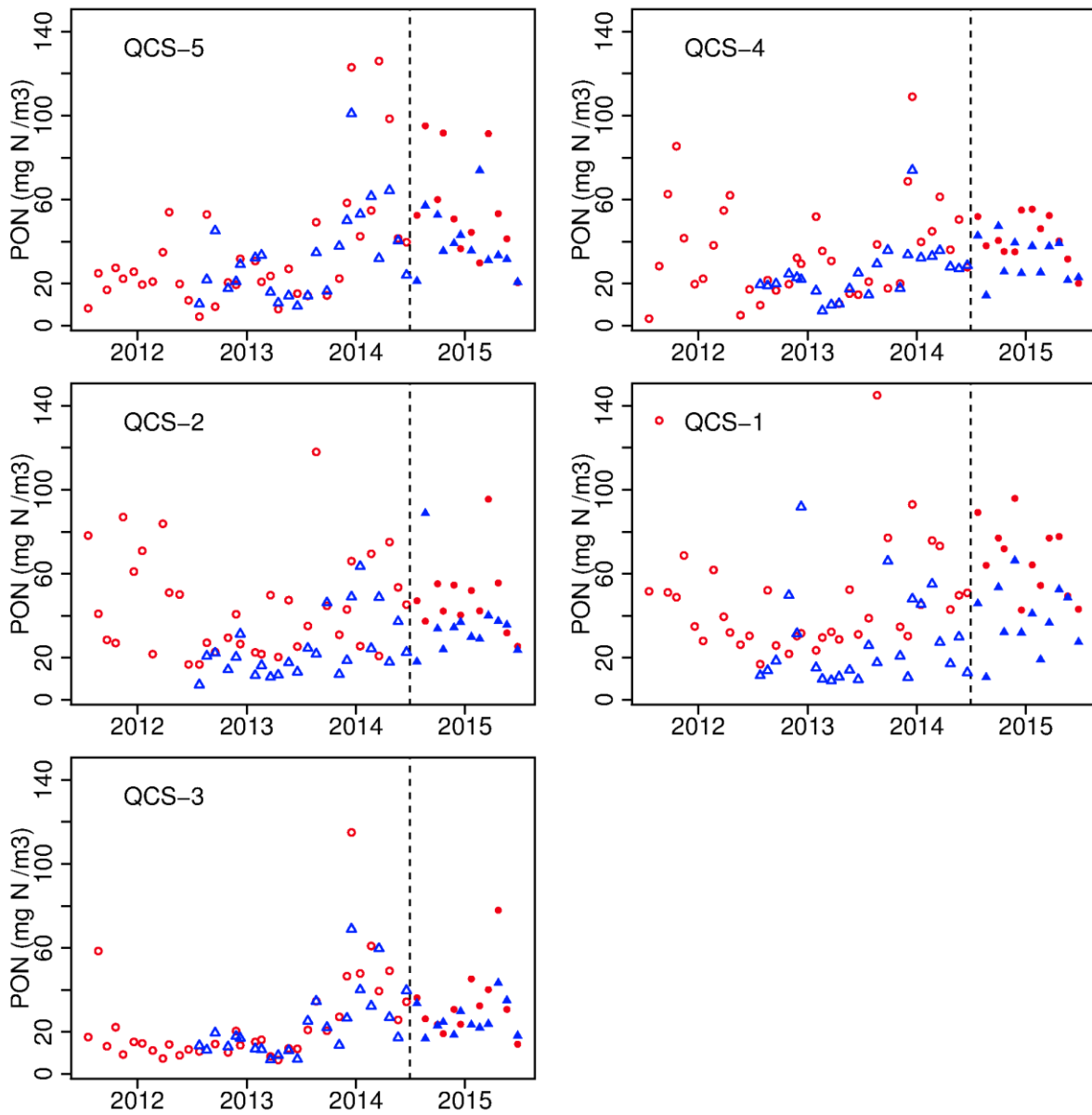
**Figure 3-15: Ammoniacal nitrogen near-surface (red) and near-bed (blue) measured at the five Marlborough District Council water-quality stations in Queen Charlotte Sound.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

### 3.13 Dissolved organic nitrogen



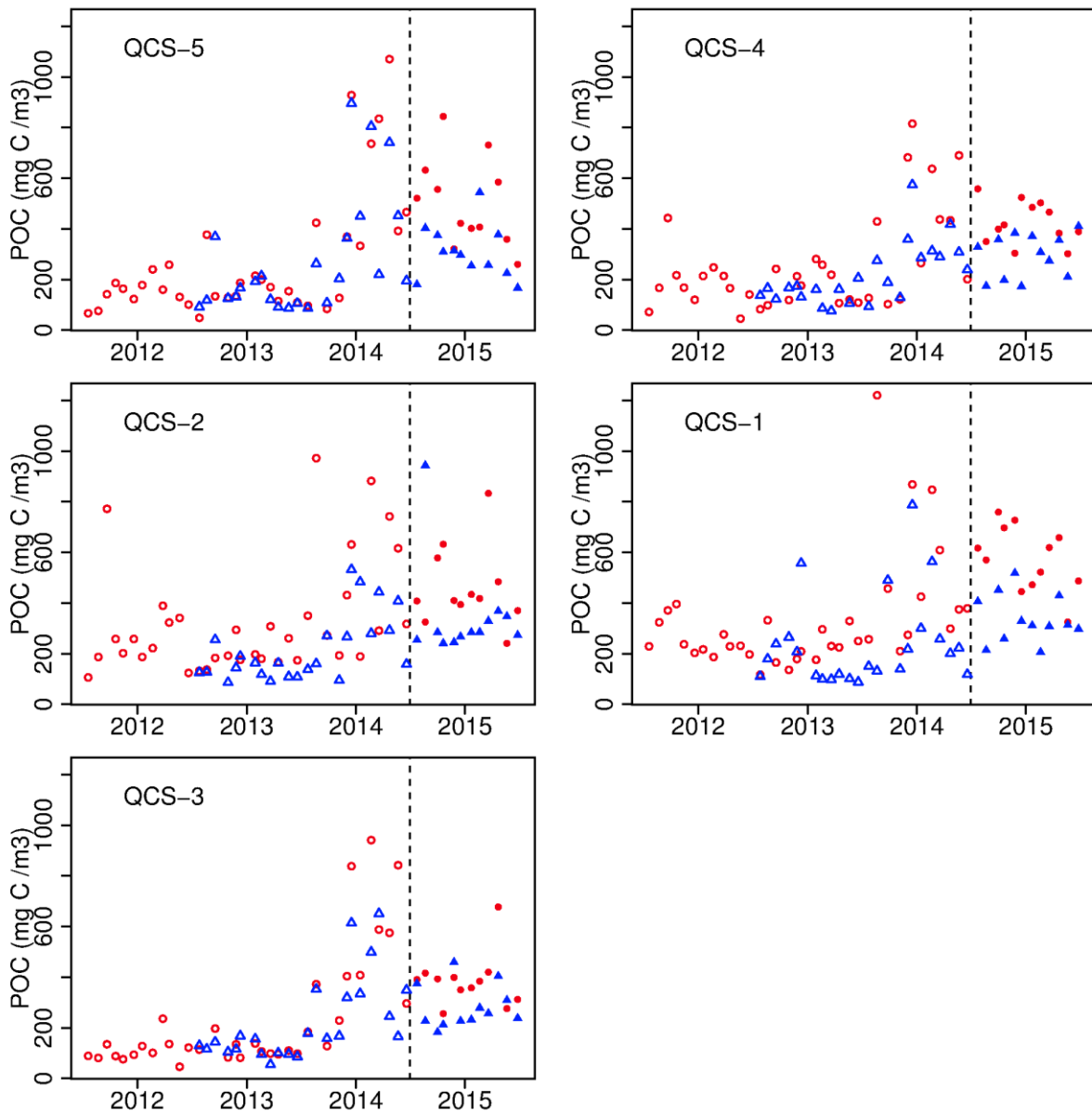
**Figure 3-16: Inferred dissolved organic nitrogen concentrations near-surface (red) and near-bed (blue) at the five Marlborough District Council stations in Queen Charlotte Sound.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

### 3.14 Particulate nitrogen



**Figure 3-17: Particulate nitrogen near-surface (red) and near-bed (blue) at the five Marlborough District Council monitoring stations in Queen Charlotte Sound.** The dashed vertical line (July 1, 2014) separates measurements of Particulate Organic Nitrogen sampled at one metre depth using a Van Dorn bottle from measurements of Particulate Nitrogen measured sampled from the upper 15 using a hose-sampler.

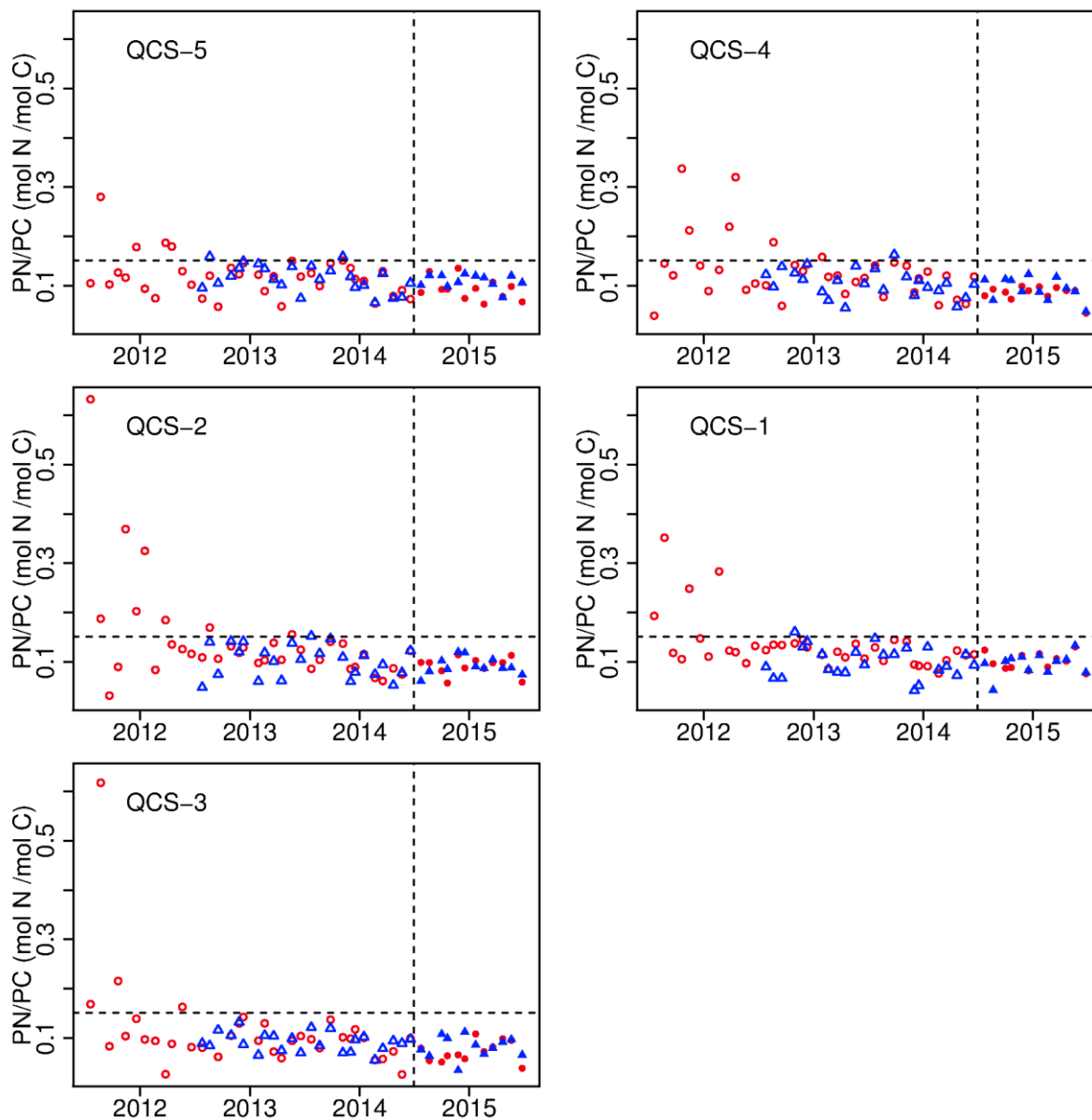
### 3.15 Particulate carbon



**Figure 3-18: Particulate carbon near-surface (red) and near-bed (blue) at the five Marlborough District Council monitoring stations in Queen Charlotte Sound.** The dashed vertical line (July 1, 2014) separates measurements of Particulate Organic Carbon sampled at one metre depth using a Van Dorn bottle from measurements of Particulate Carbon measured sampled from the upper 15 using a hose-sampler.

### 3.16 PN:PC

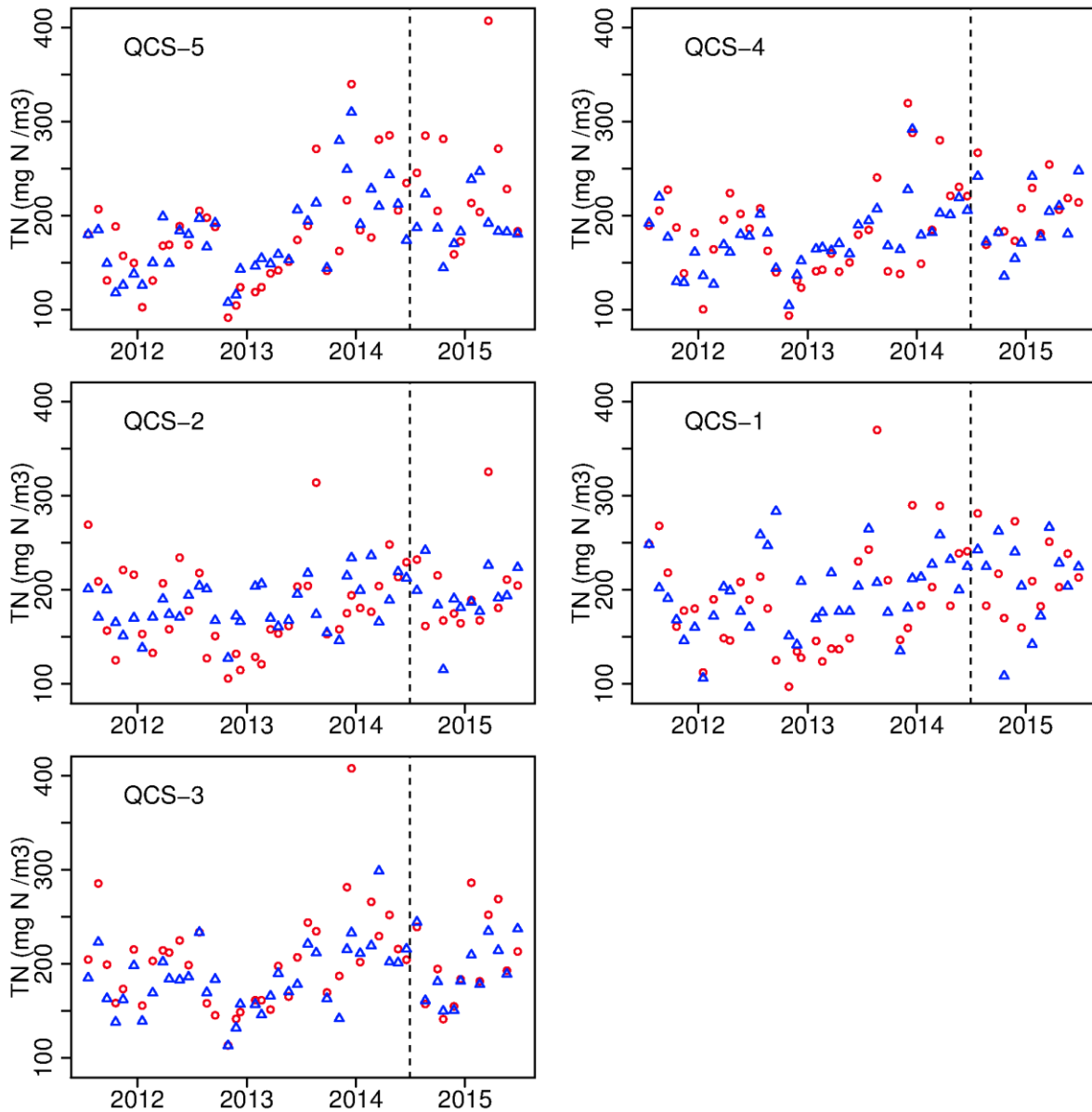
In comparison with terrestrial particulate organic matter, fresh marine particulates (living plankton and freshly dead plankton) tends to have a high N:C content.



**Figure 3-19: PN:PC ratios in near-surface (red) and near-bed (blue) samples at the Marlborough District Council sampling sites in Queen Charlotte Sound.** The vertical dashed line (1 July, 2014) separates measurements of Particulate Organic Carbon sampled at one metre depth using a Van Dorn bottle from measurements of Particulate Carbon measured sampled from the upper 15 using a hose-sampler. The horizontal dashed line represents the so-called 'Redfield ratio' (empirically determined N:C ratio for particulate material in oceanic waters).

### 3.17 Total nitrogen

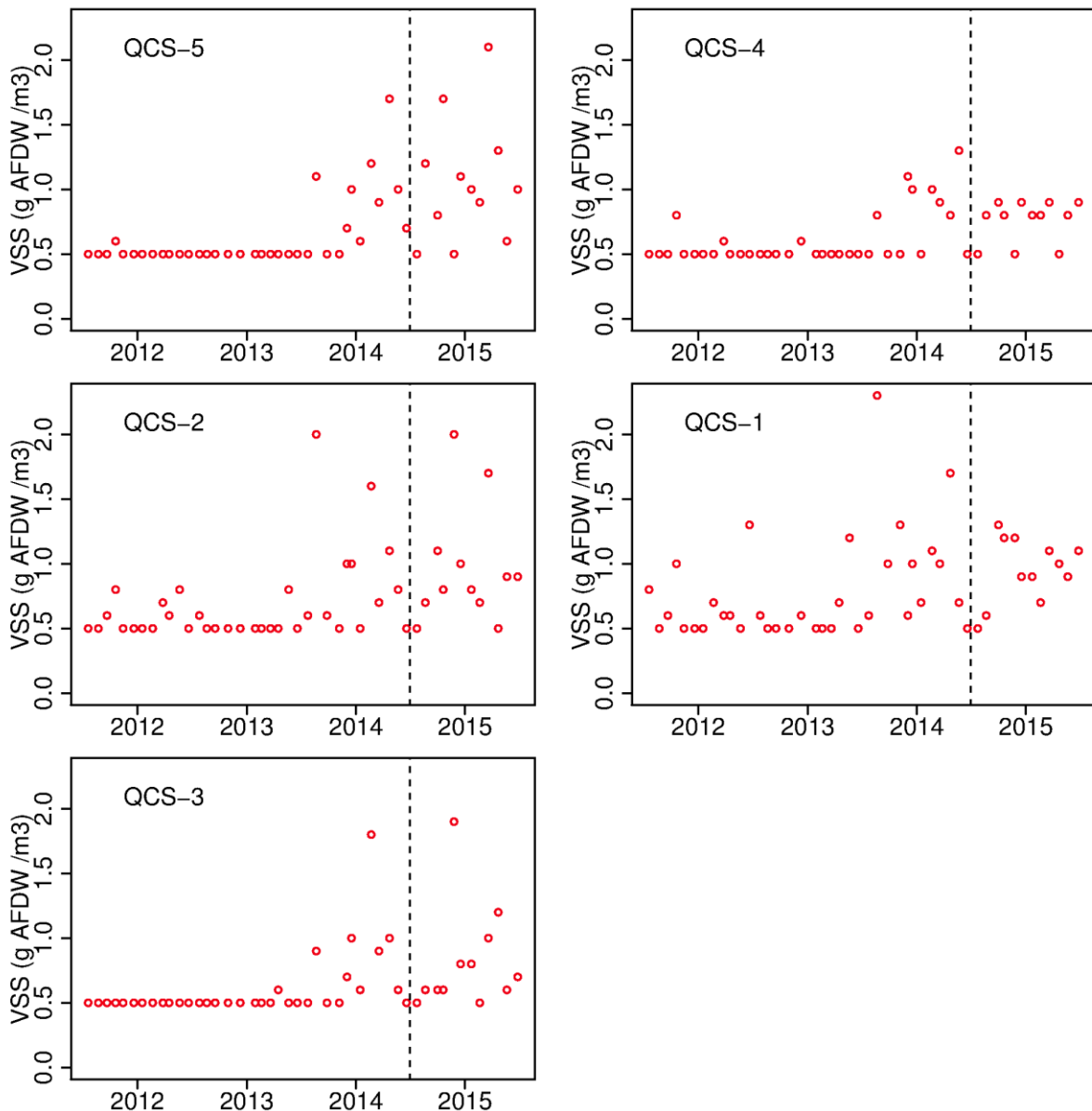
Here, total nitrogen is determined as the sum of particulate and total dissolved nitrogen.



**Figure 3-20: Total nitrogen in near-surface (red) and near-bed (blue) water measured at the five Marlborough District Council sampling sites in Queen Charlotte Sound.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

### 3.18 Volatile Suspended Solids

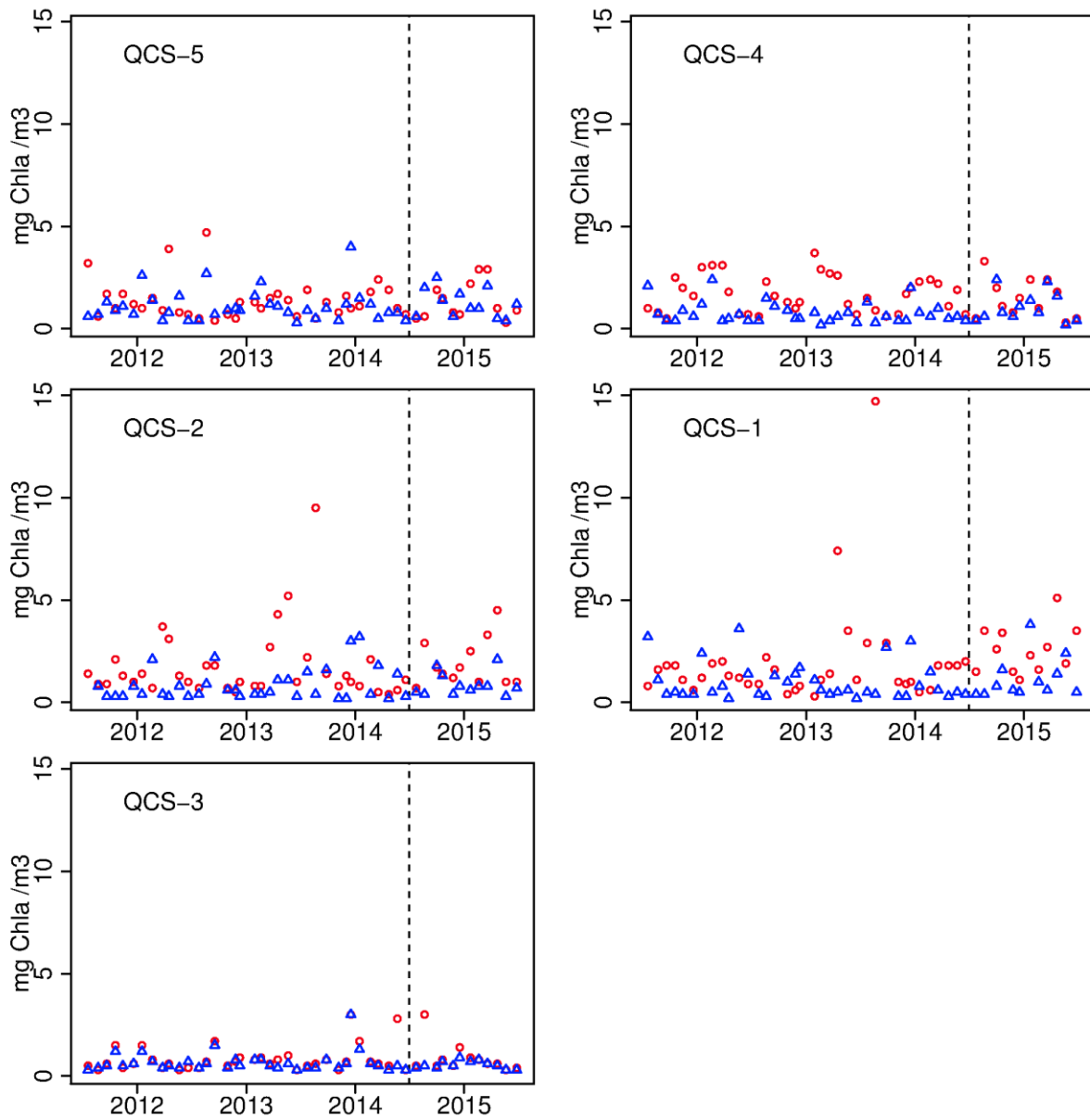
Whilst both carbon and nitrogen are components of volatile suspended solids, VSS concentration is measured independently of P(O)C and P(O)N. Thus, VSS provide an alternative/independent (to POC and PC) measure of the abundance of particulate organic matter.



**Figure 3-21: Volatile suspended solids concentrations measured in the near-surface waters at the five Marlborough District Council sites in Queen Charlotte Sound.** The detection limit for VSS is 0.5 g Ash Free Dry Weight m<sup>-3</sup>. Values that were recorded as "<detection" have been plotted as 0.5 g AFDW m<sup>-3</sup>. The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

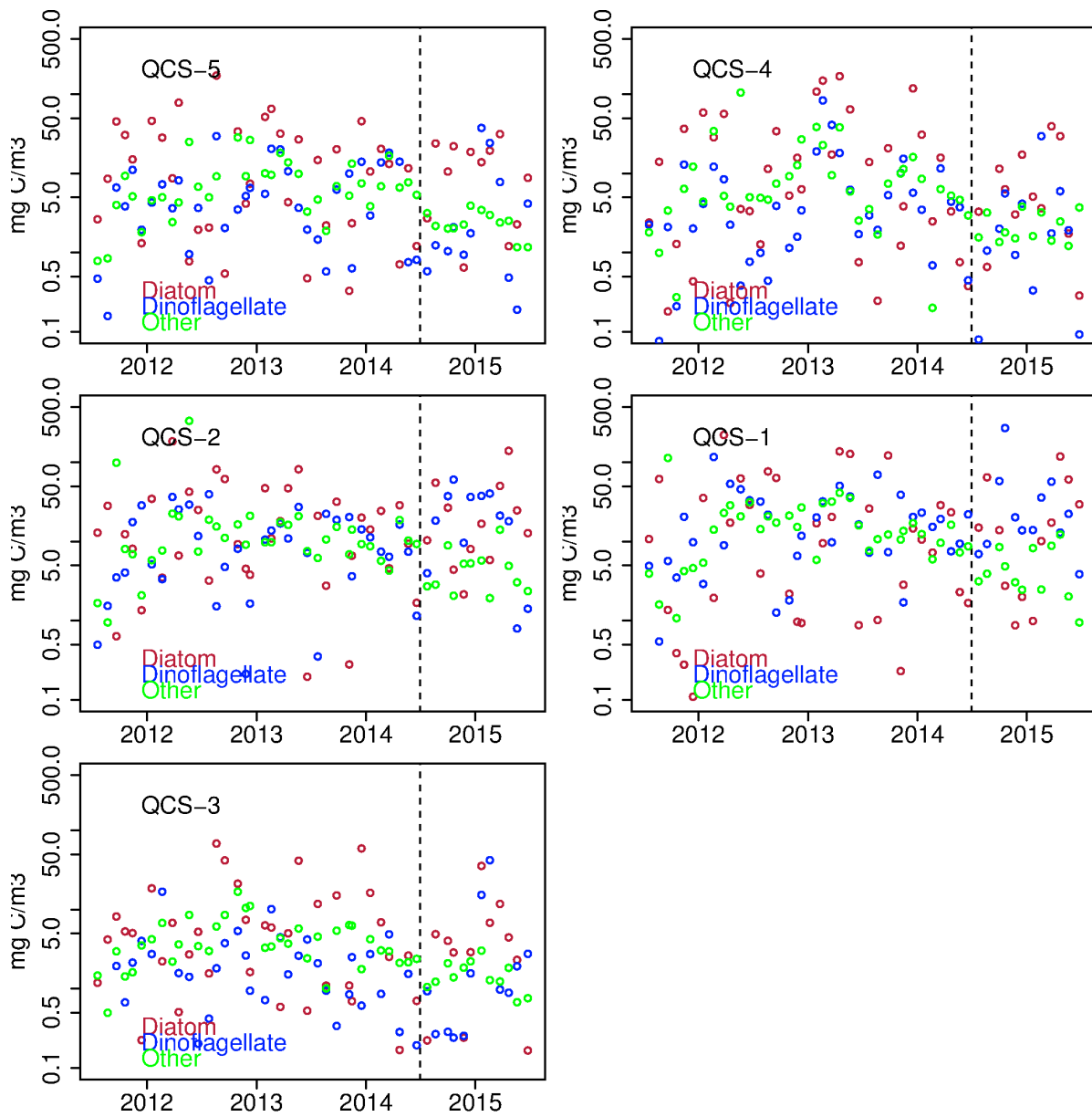


### 3.19 Chlorophyll



**Figure 3-22: Chlorophyll concentrations measured near-surface (red) and near-bed (blue) at the five Marlborough District Council stations in Queen Charlotte Sound.** Chlorophyll was measured on a GF-C filter (1.2  $\mu\text{m}$  nominal pore size). The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

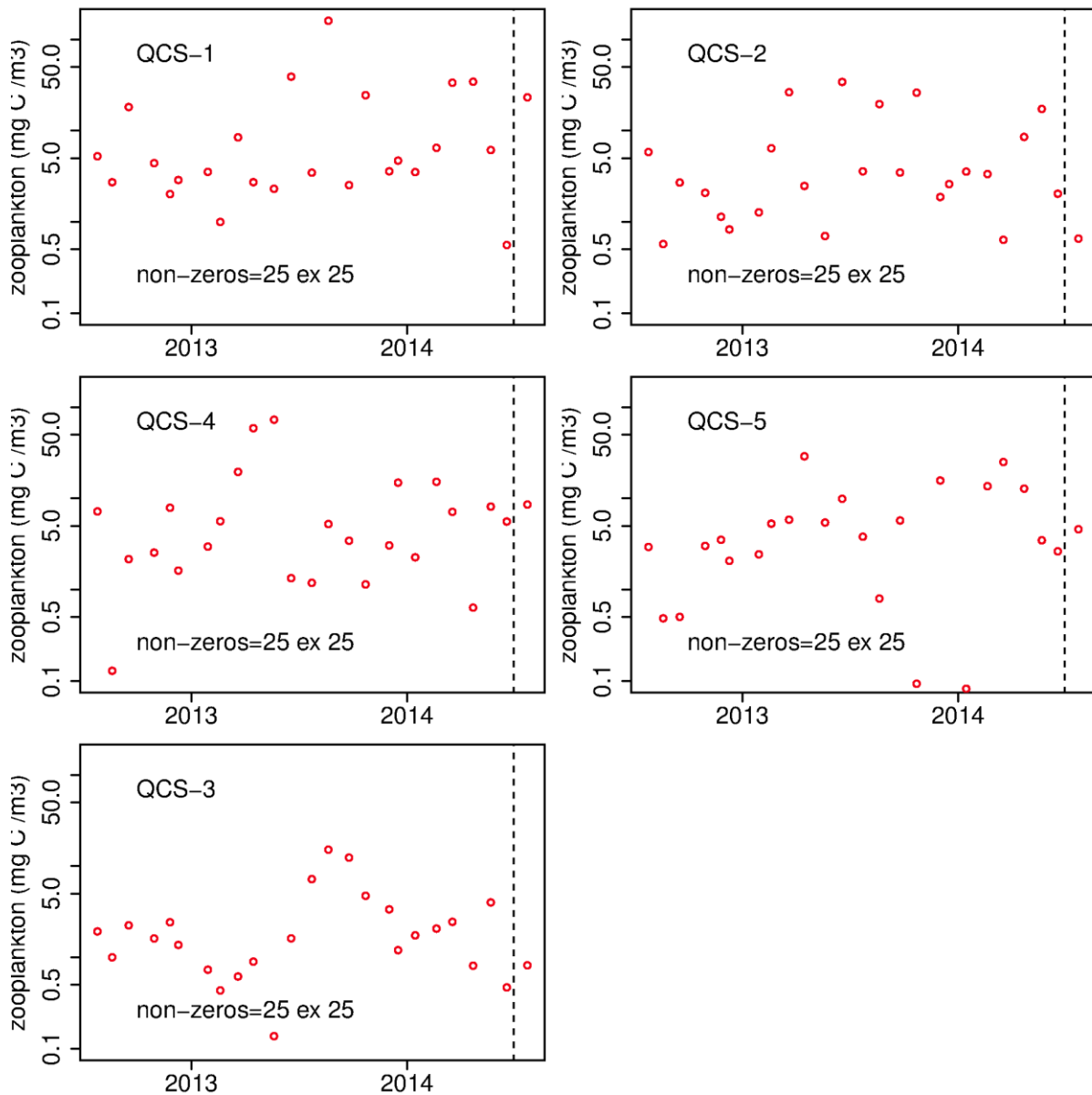
### 3.20 Algal carbon



**Figure 3-23: Phytoplankton carbon concentration from cell counts and cell dimensions at the Marlborough District Council stations (near surface water samples) in Queen Charlotte Sound.** Red symbols: diatoms; blue symbols: dinoflagellates; green symbols: other taxa. The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

### 3.21 Zooplankton carbon

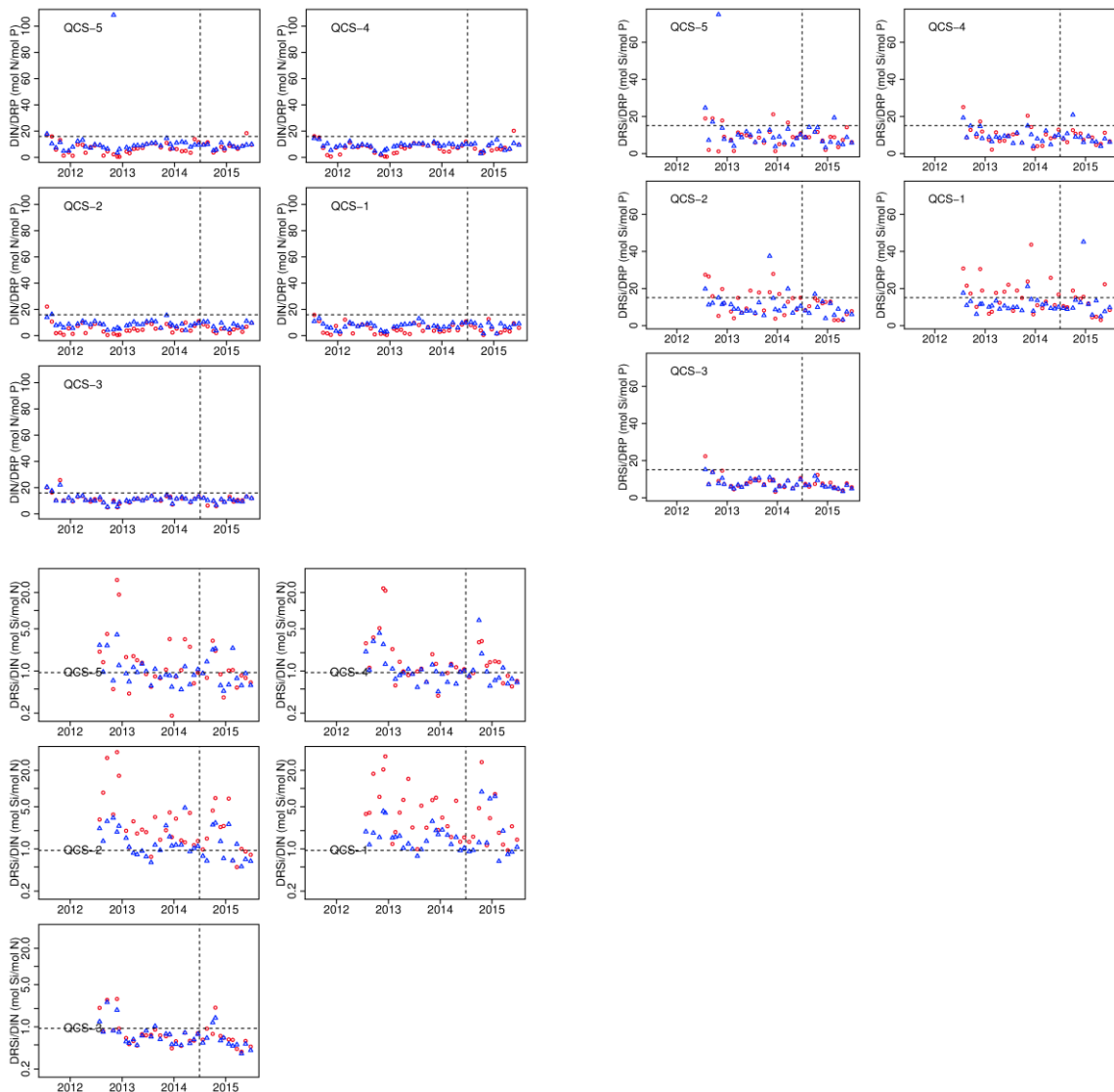
Zooplankton were counted only during two of the years for metazoans (multi-cellular). Biomass estimates are from counts, and measurements of the dimensions of a few, representative individuals. The size range spanned by different individuals of any given taxa can be very large (depending upon developmental stage). Thus, the biomass estimates are extremely imprecise (qualitative).



**Figure 3-24: Zooplankton biomass inferred from counts and dimensions at the five Marlborough District Council sites (near surface water samples) in Queen Charlotte Sound.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

### 3.22 Elemental ratios

DIN and DRSi are invariably more limiting than DRP at all sites. At sites QCS-1 and QCS-2, DIN is usually more limiting than DRSi (especially in surface waters). At sites QCS-3, DRSi is usually more limiting than DIN. Sites QCS-4 and QCS-5 are sometimes N-limited and sometimes Si-limited. Note, that in the context of these plots, the limiting element is the one which would first become exhausted if growth were allowed to continue for sufficiently long (i.e., the elemental resource that will become exhausted first). This long-term limiting element may not be the resource (or even the element) which most limited/constrained the instantaneous growth of the algae at the sampling instant.



**Figure 3-25: Ratios of dissolved inorganic nutrients measured near-surface (red) and near-bed (blue) at each site in Queen Charlotte Sound.** The horizontal dashed line indicates the Redfield ratio for the pair of elements in question. When the symbols lie below the line, the element in the numerator of the quotient expressed in the y-variate is the more limiting of the two. If the symbols lie above the line, the element in the denominator of the quotient is the more limiting. The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

### 3.23 PAR attenuation coefficient

Plant and algal growth is crucially dependent upon light-energy. Thus, the extent to which incoming light is attenuated as it descends through the water-column is a key determinant of the productive capacity of the a water-body and the surface of the underlying bed. The attenuation coefficient for photosynthetically active radiation (PAR) is an empirical property of a water-column that is indicative of how rapidly PAR intensity declines with increasing depth below the water-surface.

The PAR attenuation coefficient is (relatively) easily measured (if one has access to a PAR sensor), but it is not a fundamental property of either the water or the material dissolved and/or suspended in the water. Rather, the attenuation coefficient is an ‘apparent’ (or emergent) property whose instantaneous value is determined by two, more fundamental properties: (a) the capacity of the water (and materials contained therein) to absorb light (absorption per unit photon travel distance), (b) the scattering properties of the water and materials therein (which increase the total photon travel distance per vertical metre traversed – thereby increasing the probability of absorbance per vertical meter travelled).

Suspended particulates induce scattering. In doing so they increase the total path length that a particle must traverse per linear metre of travel. Since the total travel distance per linear meter increases, the probability of absorbance per linear metre also increases. As a result, light intensities tend to decline more rapidly with increasing depth-below-surface in high turbidity waters than in low turbidity waters.

Numerous materials (incl. pure water) absorb photons. Each material has a unique absorbance spectrum (i.e., absorbs some colours of light more readily than others). Water absorbs reddish hues much more readily than blueish ones. Chlorophyll molecules absorb strongly at the two ends of the visible spectrum (red/orange and blue/violet) but weakly in the intervening yellow/green range. Tannins (e.g., from leachate emanating from afforested catchments) tend to absorb blues and greens more readily than reds and oranges.

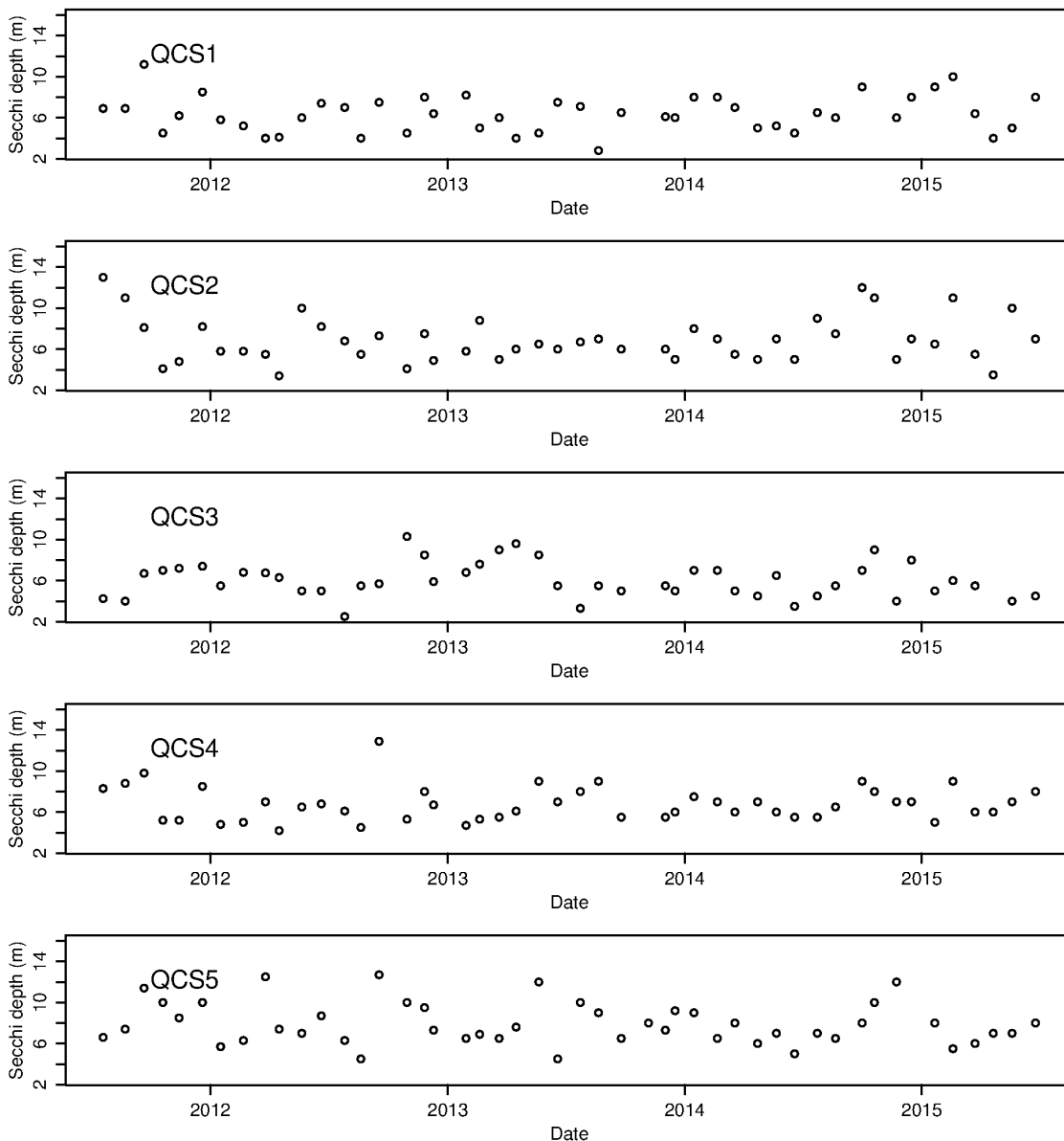
Depth profiles of PAR have not been measured as a part of the MDC monitoring program – however Secchi disk depths (see below) have been and these may provide a proxy for PAR attenuation.

### 3.24 Secchi disk depth

Secchi disk measurements provide a crude measurement of water clarity. Clarity is influenced by two factors: (a) the probability (per unit straight-line travel distance) that a photon will encounter a reflective object (i.e., the scattering properties of the water), (b) the absorbance properties of the water. Not surprisingly, PAR attenuation coefficients and Secchi disk depths are often correlated – however the correlation is often poor. In part, this is because Secchi disk depth measurements are imprecise. Water clarity is one determinant of this distance, but there are many other confounding determinants. These include: the visual acuity of the observer, the surface state (smooth, choppy etc.) of the water, degree of cloud-cover, elevation of the sun, ship-shadow effects etc.). Despite the poor precision of Secchi disk measurements, they are a common part of many water-quality monitoring programmes. They do not require expensive/difficult to maintain equipment and they are quick/easy to make. Perhaps more importantly, the Secchi Disk depth has greater intuitive meaning to a lay-person than a measure such as concentration of suspended solids, or chlorophyll.

Secchi disk depths have ranged from a little more than 2 m to about 12 m with most values being in the range 4-8 m (Figure 3-26). Site QCS-5 tends to have the greatest Secchi disk depths. World-wide,

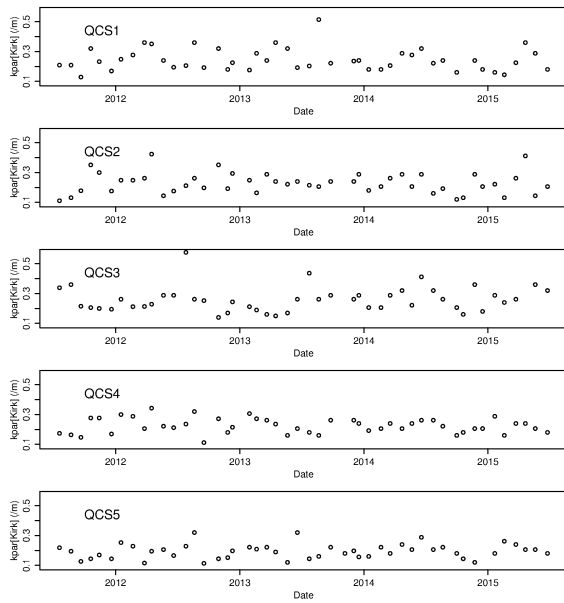
Secchi disk depths range from a few cm in very turbid waters to (exceptionally) several tens of metres (Antarctic waters) but Secchi disk depths in the range 2-10 m are the norm. The majority of Secchi disk depths in Queen Charlotte/Tory Channel fall within that range (and none are < 2 m).



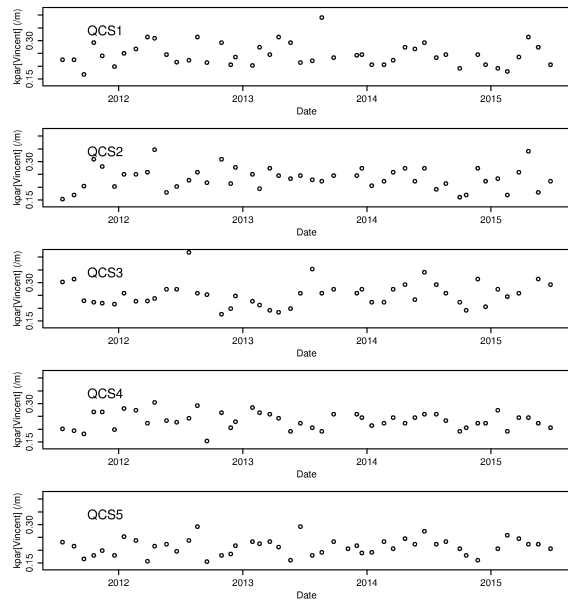
**Figure 3-26: Secchi disk depth measured at the five sites in Queen Charlotte Sound and Tory Channel.**

As noted above, measurements of Secchi disk depths provide a (often poor) proxy measure from which the PAR attenuation coefficient may be derived by exploiting empirical relationships. Kirk (1983) provides one such empirical relationship based upon international data. Vincent, Howard-Williams et al. (1989) provide data (from Pelorus Sound) that enable an alternative (perhaps more appropriate) relationship to be derived.

### Kirk relationship



### Vincent, Howard-Williams et al. relationship



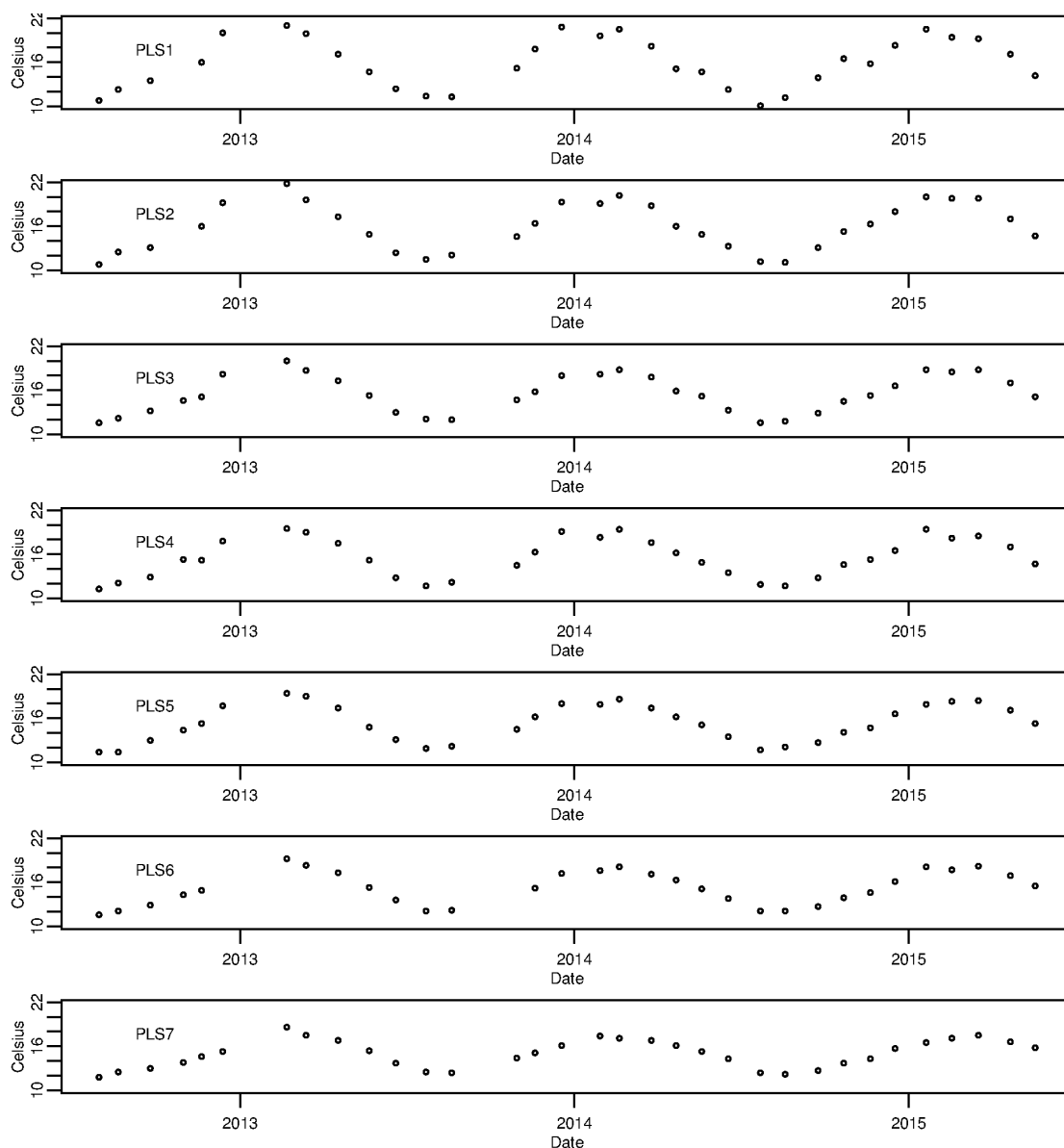
**Figure 3-27: PAR attenuation coefficients inferred using the relationship described in Kirk (left panels) and the data of Vincent et al. (right panels in Queen Charlotte Sound).**

## 4 Results (Pelorus Sound)

### 4.1 Temperature

#### 4.1.1 Hand-held surface temperature

The phase of the annual temperature cycle is similar at all sites and in all years (Figure 4-1). The winter minimum occurs around August and the summer maximum around February. The winter minima are around 10-11 °C at the inner Sound sites and around 12 °C at the outer sites. During the summer, the inner Sound sites are warmer (circa 21 °C) than the outer Sound sites (circa 18 °C).

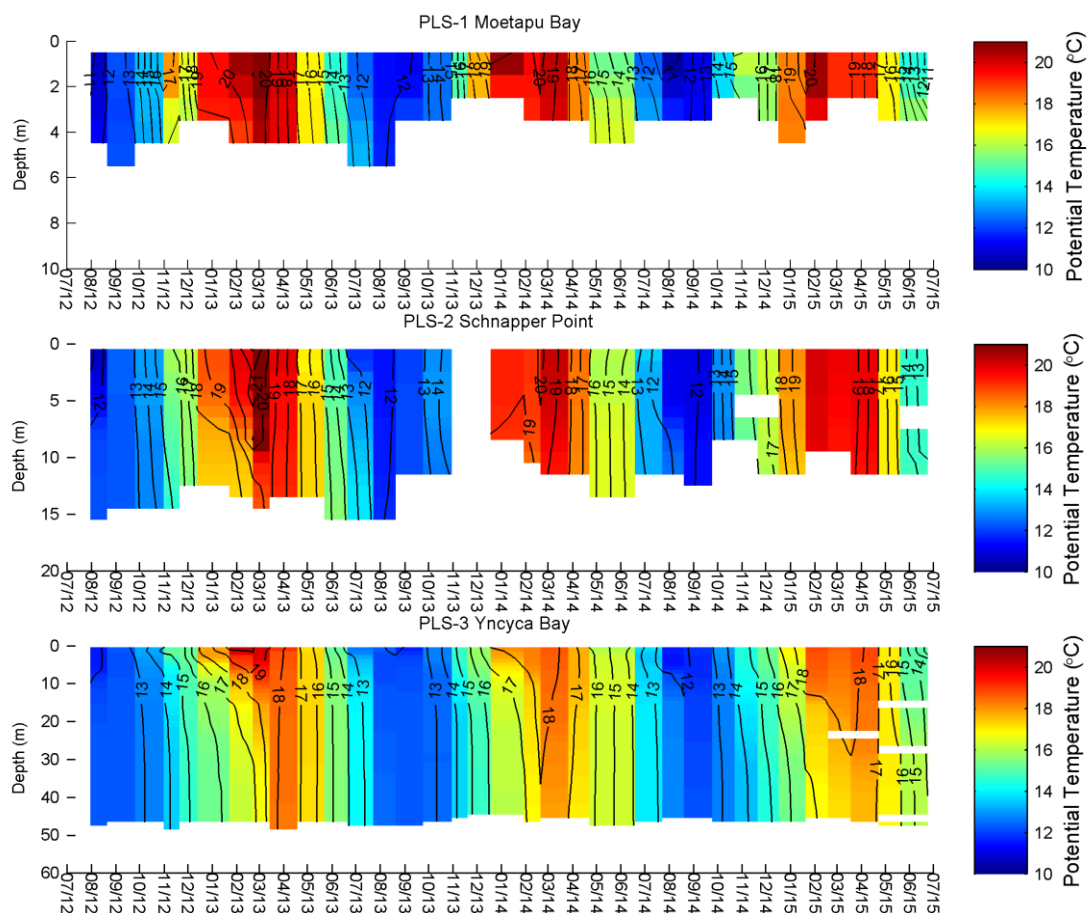


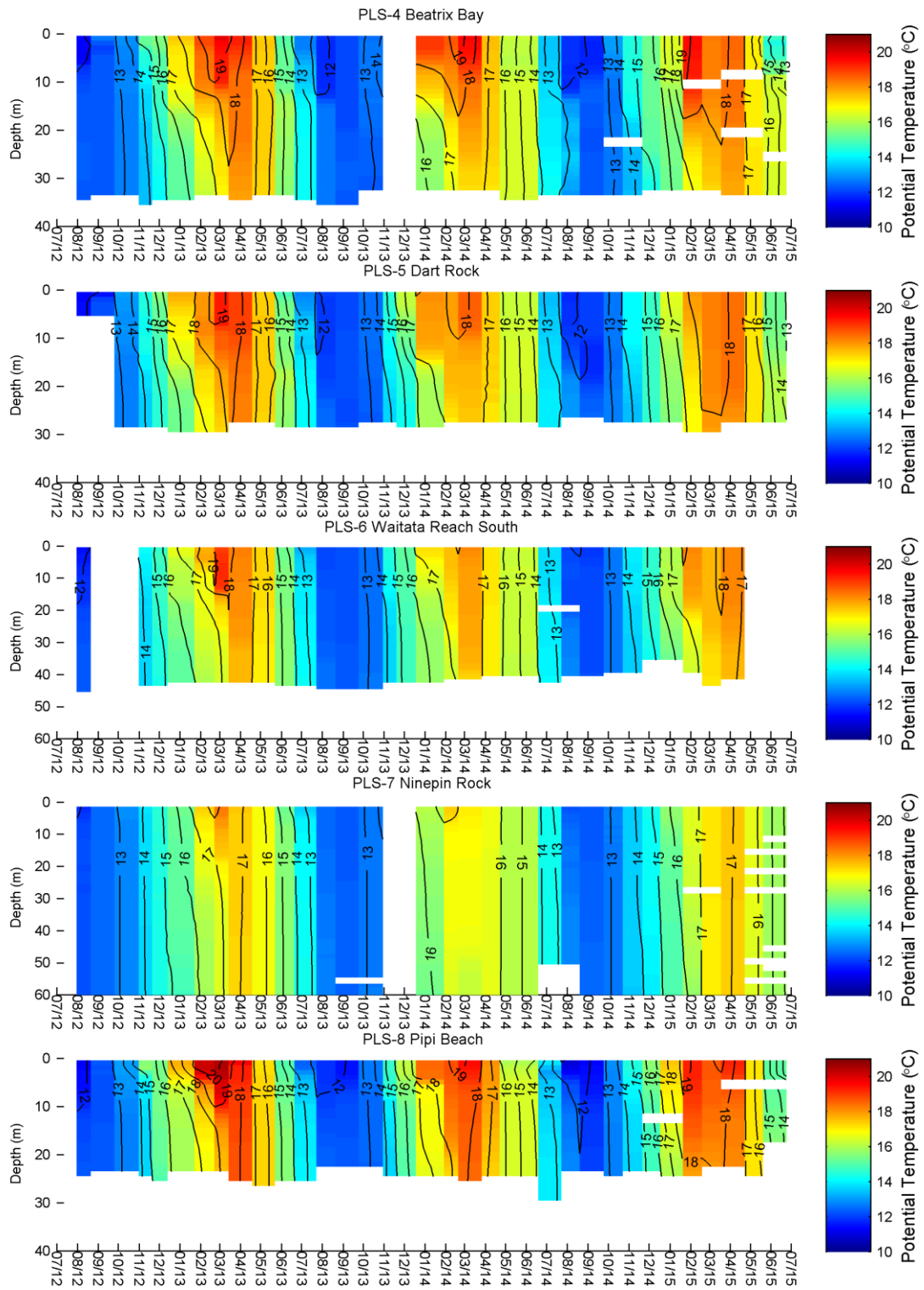
**Figure 4-1: Near surface water temperature measured with a hand-held probe at each of the seven Marlborough District Council Pelorus water quality sampling stations. Data from January and September 2014 were rejected as being unreliable.**

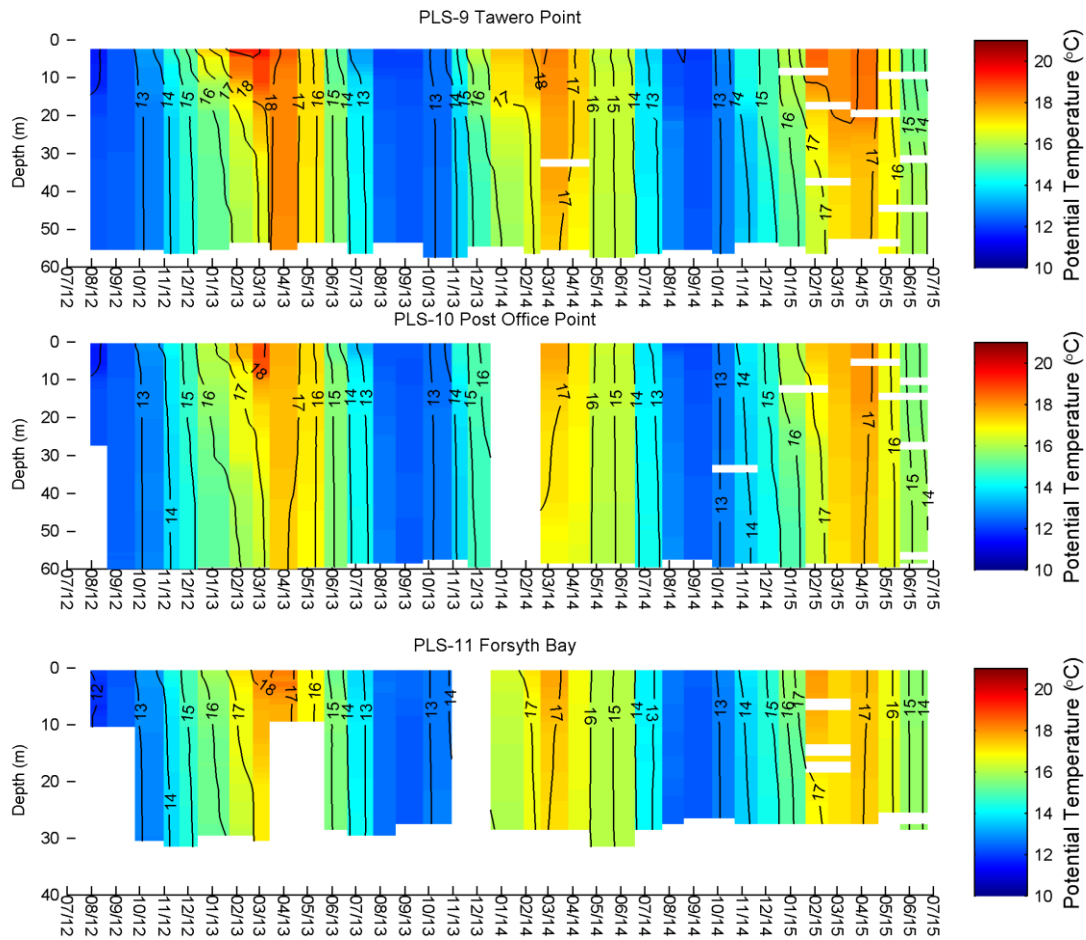


### 4.1.2 CTD temperature profiles

The seasonal variations in temperature throughout the sounds are evident in the temperature-by-depth-and-time colour plots (Figure 4-2). Temperatures are coolest (around 12°C) between July and September, and warmest February-March. The highest temperatures are recorded at the surface in the inner sounds PLS-1, 2, 3 and 8 with in excess of 21°C recorded at PLS-2 in March 2013. Summer-time surface temperatures generally decrease further outward in the sound with the outward most site PLS-7 peaking at 17-18°C. Summer thermal stratification occurs at many sites, particularly PLS-3, 4, 5, and 8. The innermost sites PLS 1 and 2 are sufficiently shallow that the surface mixed layer extends full depth in summer so the stratification is not evident. The intermediate sites PLS-6 and 9 show weaker stratification, which is reduced further at the outer sites 7, 10 and 11 which remain mixed most of the year. During the winter period, most sites are well mixed. However some of the innermost sites show surface cooling (PLS-1, 3, 4, 5 and 8). Cooler waters are normally denser than warmer water and sink, however the lower salinity of surface waters during winter (see below) has a stronger influence on density.





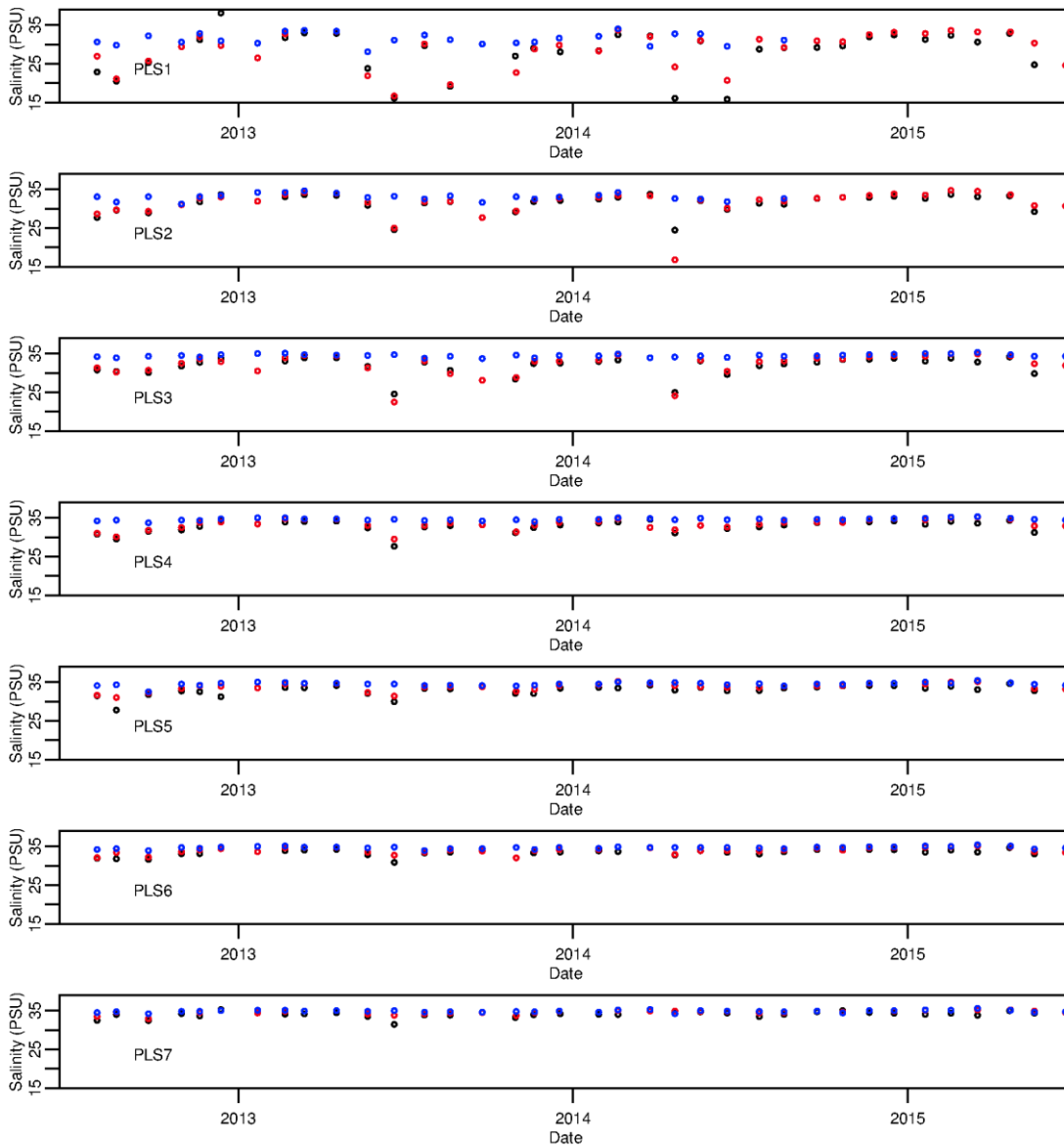


**Figure 4-2: Contour plots of evolving depth profiles of temperature through time at the Pelorus stations.** Data are from the monthly CTD casts. White space indicates missing/rejected data (or the maximum depth to which the cast extended).

## 4.2 Salinity

### 4.2.1 Hand-held surface salinity & laboratory determinations

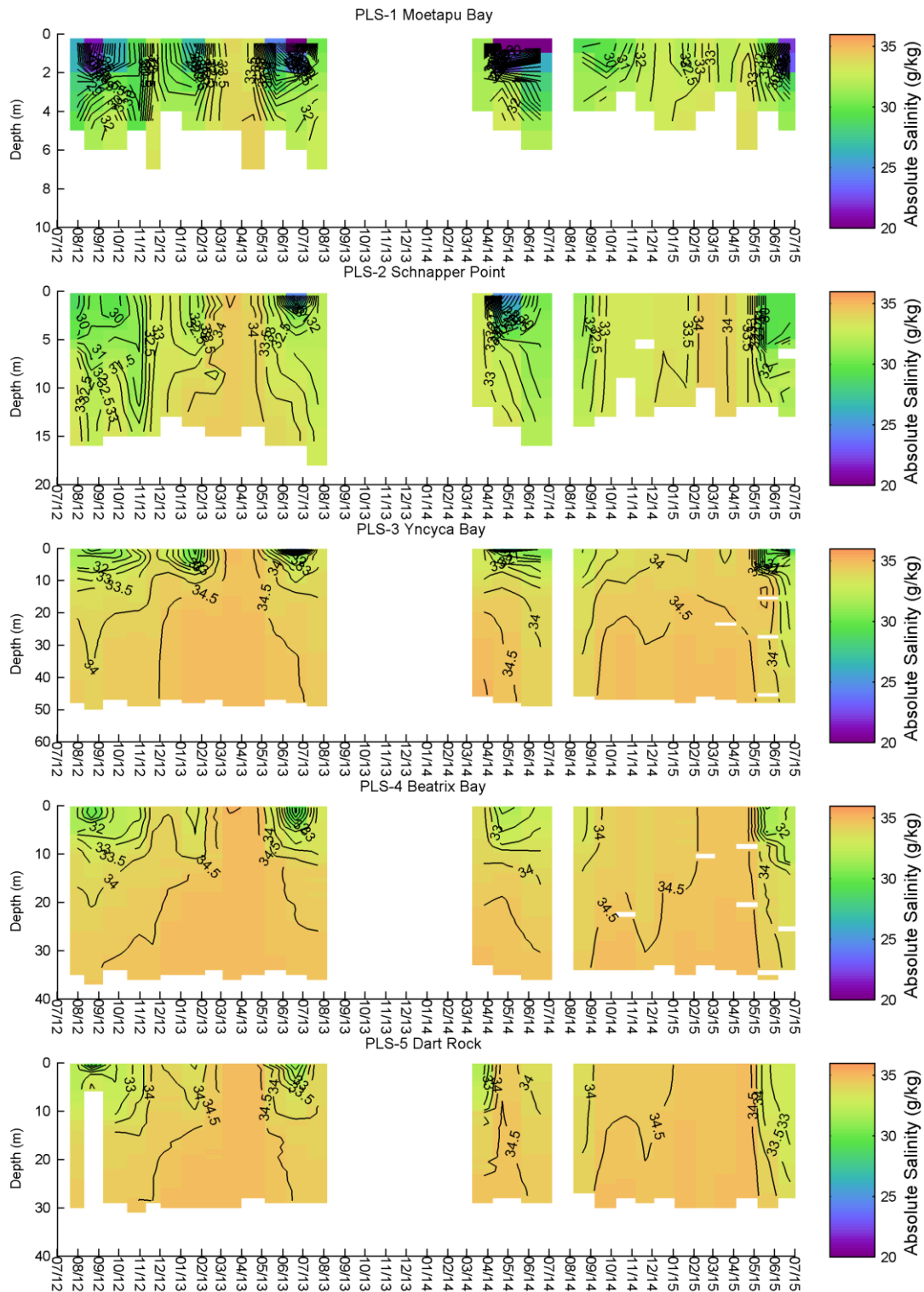
As one might expect, near surface salinities tend to be a little lower than near-bed ones (Figure 4-3). Near surface salinities measured at sea are very similar to those subsequently recorded in the lab. Near surface salinities dropped below 20 PSU in inner Pelorus (presumably, following high rainfall events in the catchment) but they have remained above 30 PSU at outer sites.

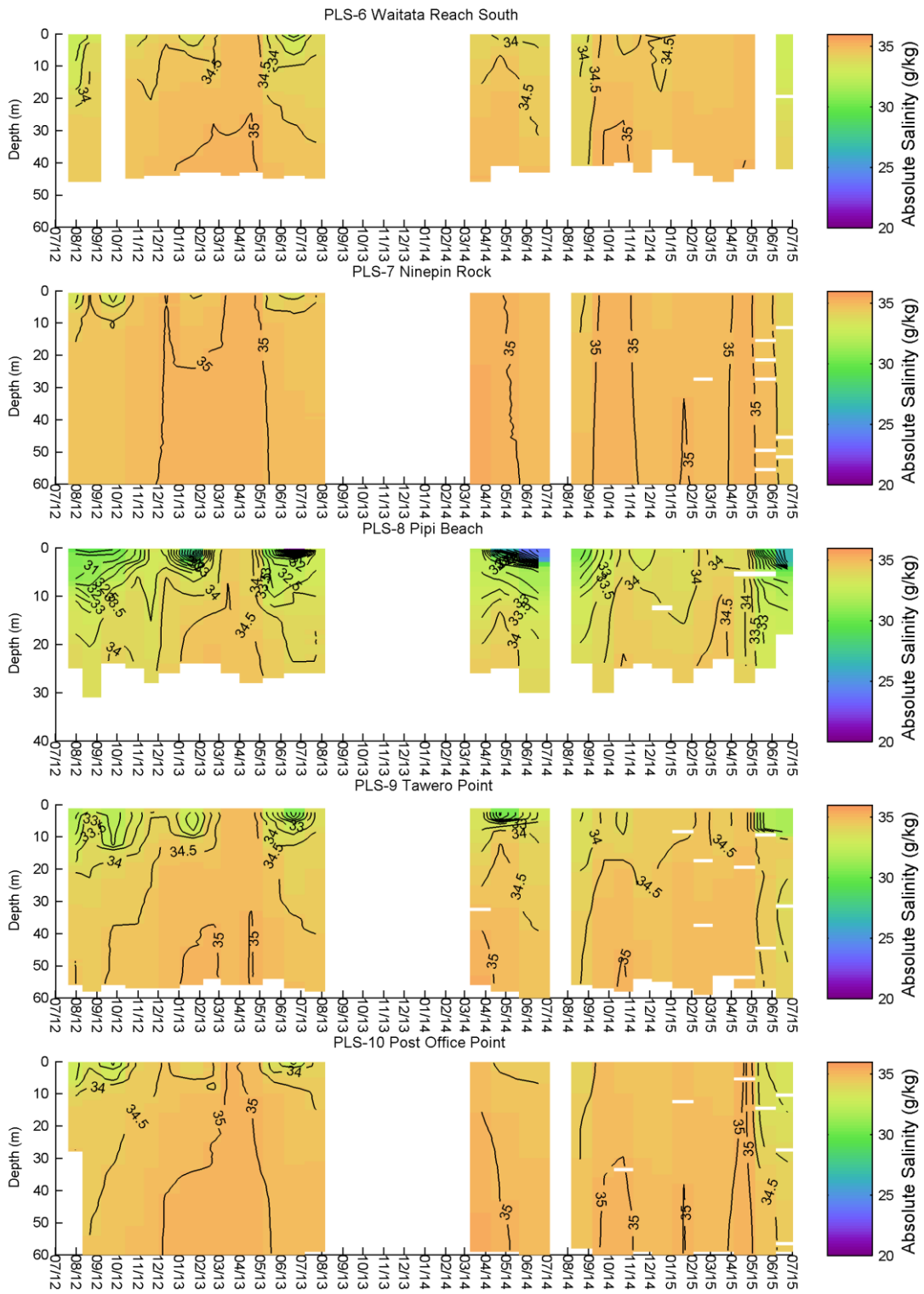


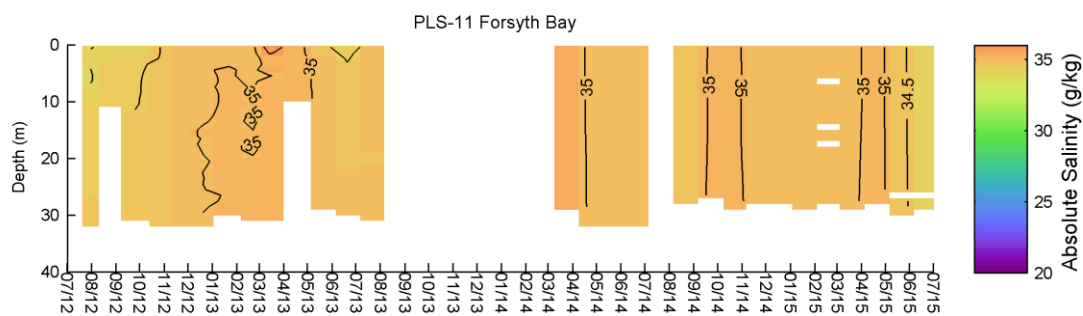
**Figure 4-3: Salinity measured at the seven Marlborough District Council sites within Pelorus. A hand-held probe was used at 1 m depth (black circles) and in water-samples were returned to the laboratory (red circles: near surface (1m or depth averaged to 15 m); blue circles: near-bed). Different instruments were used to measure salinity at sea and in the laboratory.**

#### 4.2.2 CTD salinity profiles

Contour plots of evolving depth profiles of salinity through time at the Pelorus stations are shown in Figure 4-4. Salinities in the Pelorus Sound vary over a larger range than in the Queen Charlotte Sound due to the influence of the Pelorus River. There is no clear seasonal trend; rather low salinity occurs in pulses throughout the monitoring period. Salinity generally has a stronger effect on density than temperature. Periods of high river discharge cause low salinity plumes that spread throughout the sound. This can be seen by the low salinity surface waters particularly at the inner sites. The salinity increases with distance through the sound as the plume mixes.





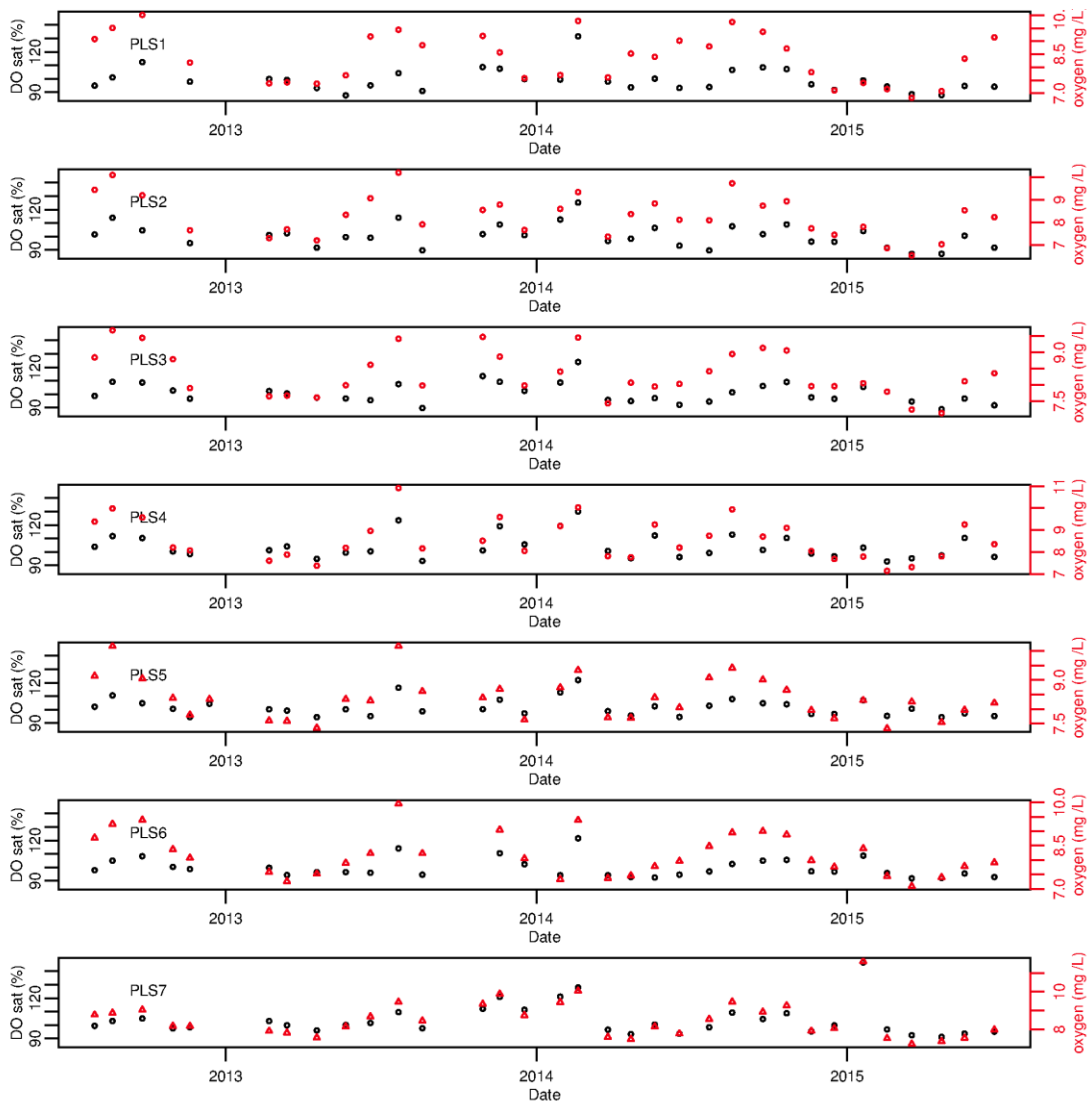


**Figure 4-4: Contour plots of evolving depth profiles of salinity through time at the Pelorus stations.** Data are from the monthly CTD casts. White space indicates missing/rejected data (or the maximum depth to which the cast extended).

### 4.3 Dissolved oxygen

#### 4.3.1 Hand-held surface oxygen saturation

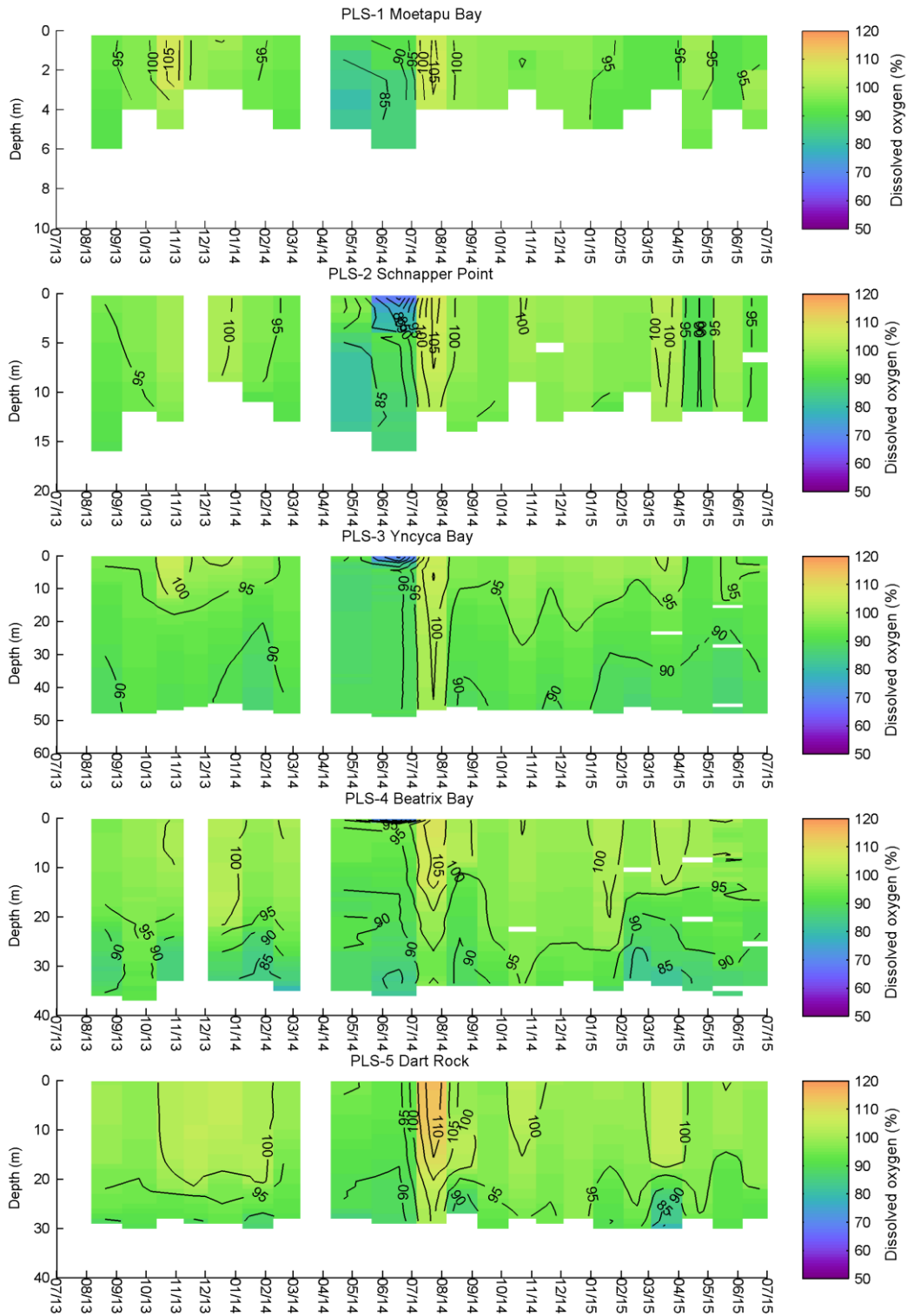
Near surface dissolved oxygen concentrations have been high (>90% saturation) at all stations throughout the sampling period (Figure 4-5). Concentrations and saturation levels tend to be highest in late-winter/early spring and lowest during the summer months.

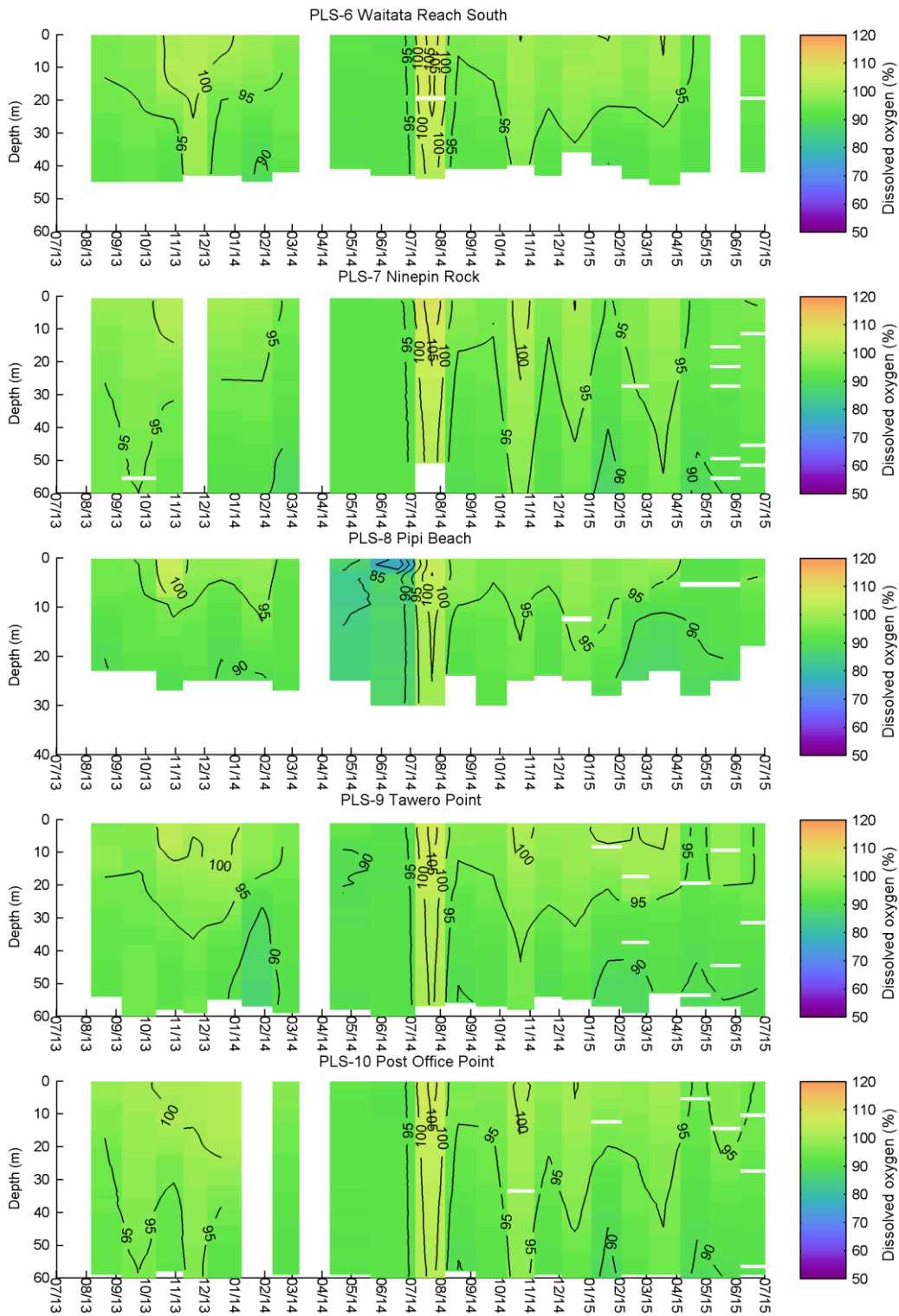


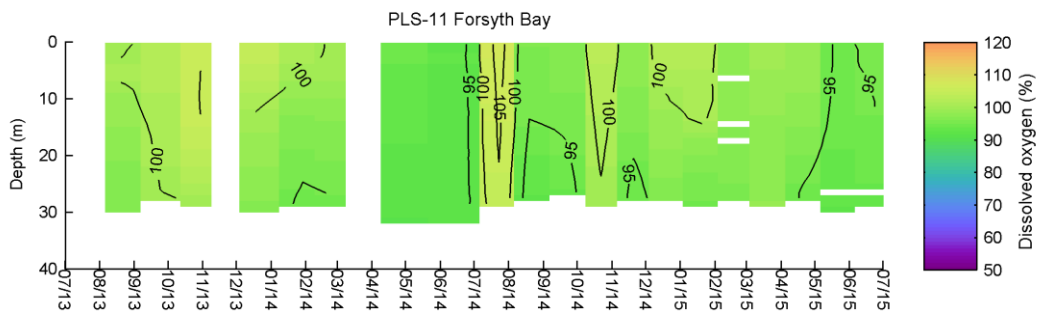
**Figure 4-5: Dissolved oxygen measured at one metre below the sea-surface at the seven Marlborough District Council Pelorus water-quality monitoring stations.** A small number of records from the hand-held sensor have been rejected as being implausibly high saturation (>140%) and concentration. Where possible, those records were replaced with near-surface readings from the CTD casts. Black symbols are oxygen saturation (left axis). Red symbols are concentration (right axis). Dissolved oxygen saturation is a function of salinity, temperature (and air pressure). Thus, the correlation with absolute oxygen concentration is strong, but imperfect.



### 4.3.2 CTD oxygen profiles

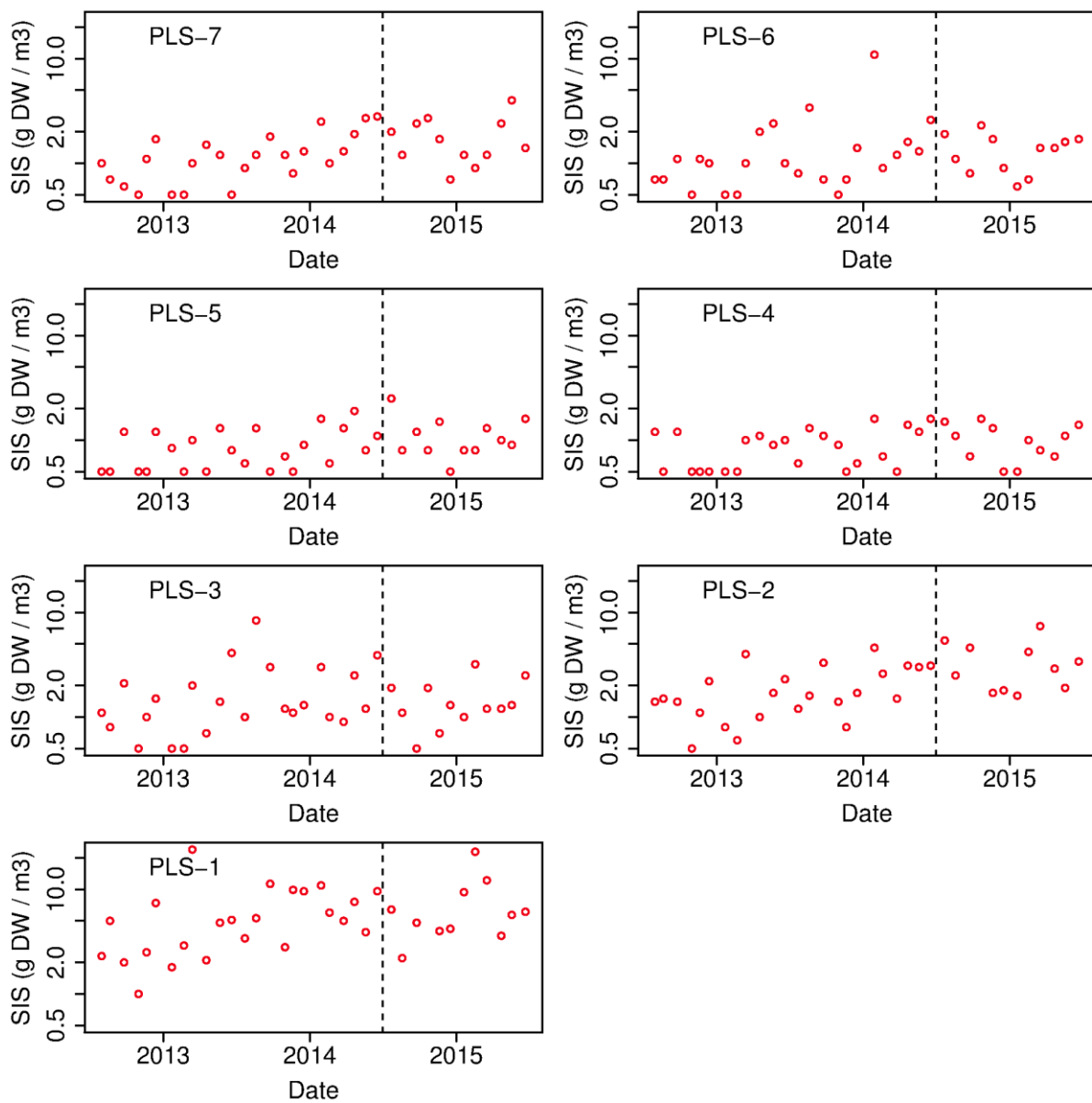






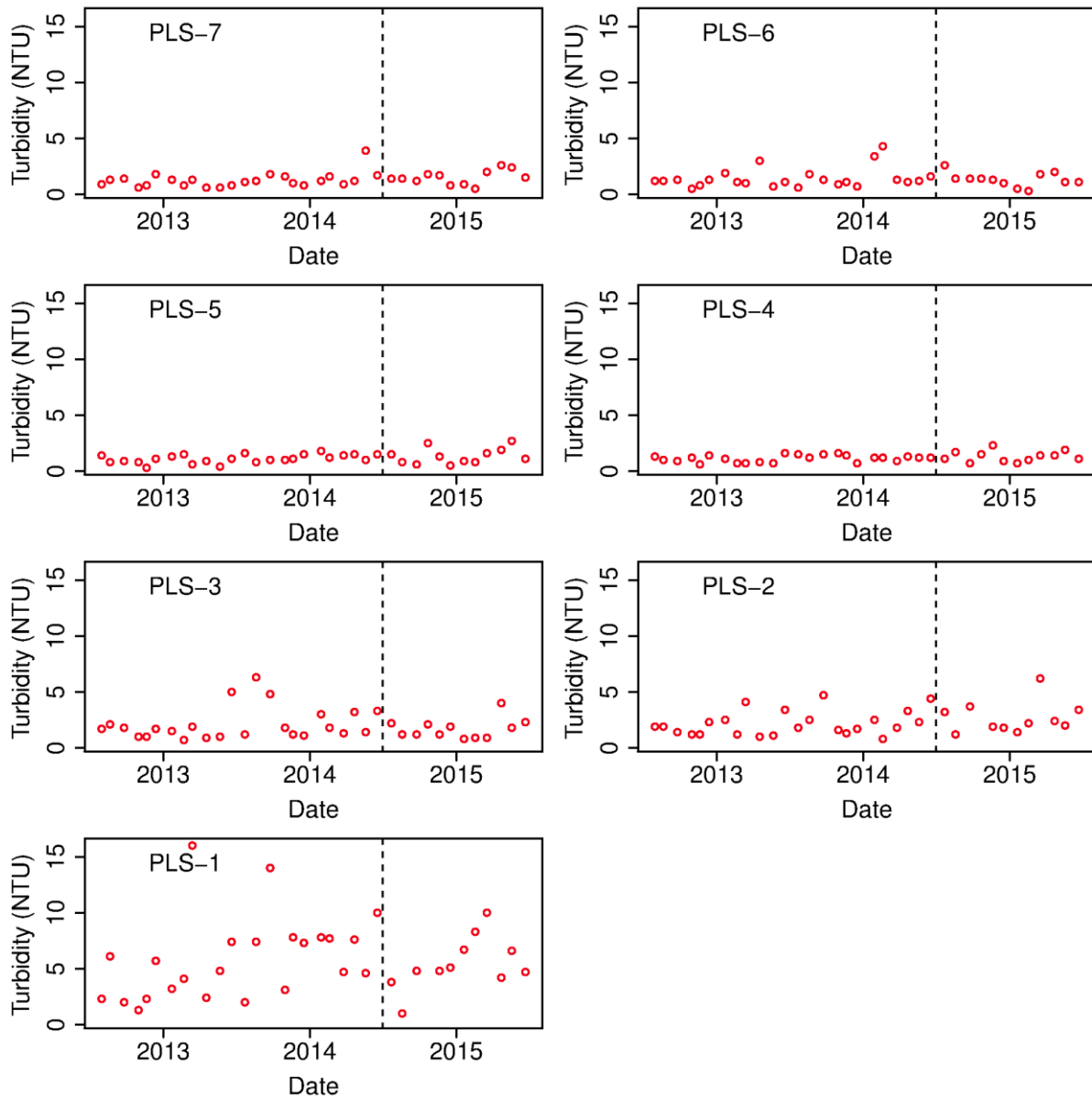
**Figure 4-6: Contour plots of evolving depth profiles of oxygen saturation through time at the Pelorus stations.** Data are from the monthly CTD casts. White space indicates missing/rejected data (or the maximum depth to which the cast extended).

#### 4.4 Suspended inorganic solids



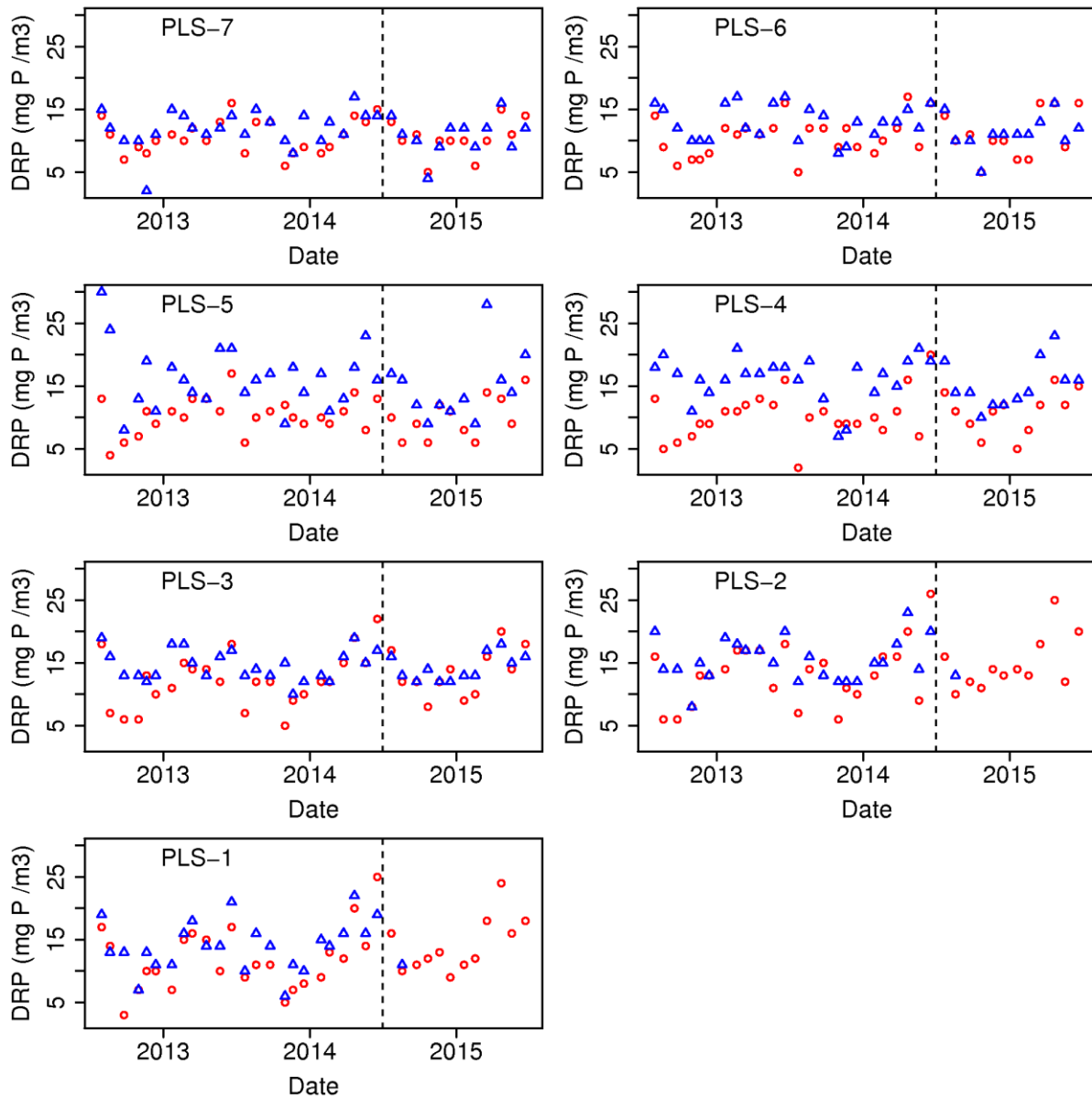
**Figure 4-7: Concentrations of suspended inorganic solids measured in the near-surface water-samples of the seven Marlborough District Council Pelorus stations.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

## 4.5 Turbidity



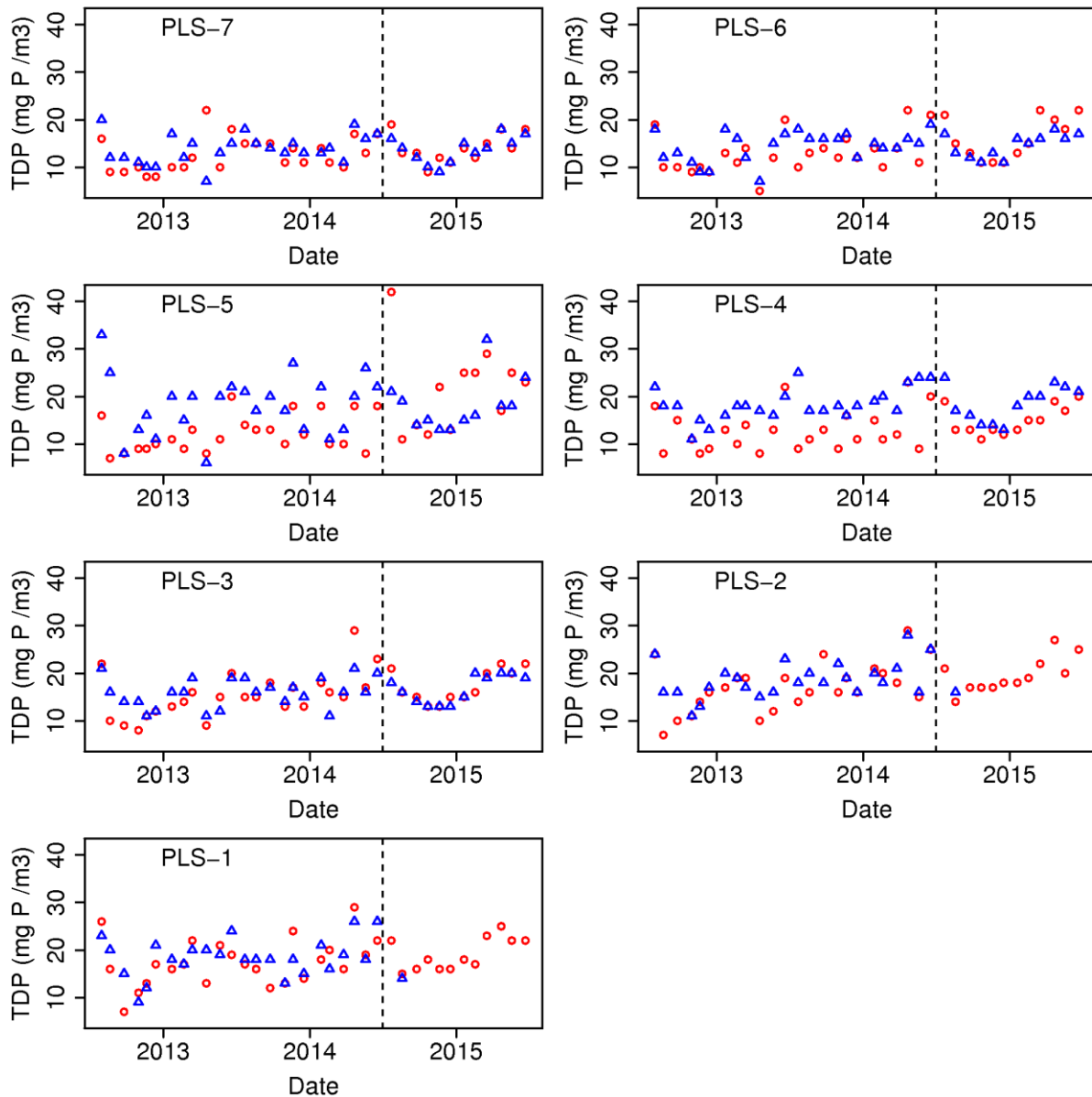
**Figure 4-8: Near-surface turbidity measured at the seven Marlborough District Council water quality monitoring sites in Pelorus.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

## 4.6 Dissolved reactive phosphorus



**Figure 4-9: Time-series of dissolved reactive phosphorus measured near surface (red) and near bed (blue) at the seven Marlborough District Council Pelorus sampling sites.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

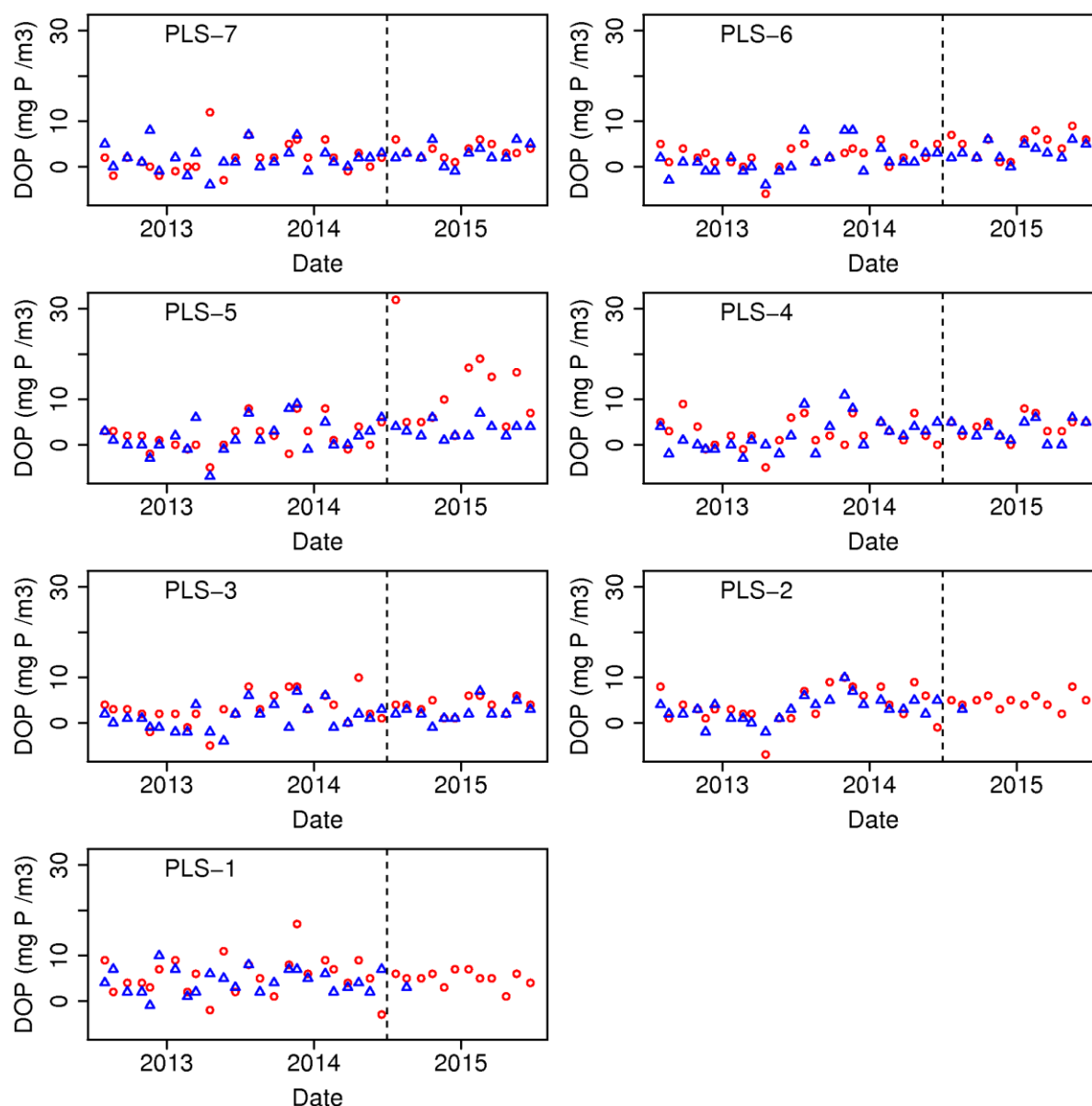
## 4.7 Total dissolved phosphorus



**Figure 4-10: Total dissolved near-surface (red) and near-bed (blue) phosphorus measured at the seven Marlborough District Council Pelorus stations.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

## 4.8 Dissolved organic phosphorus

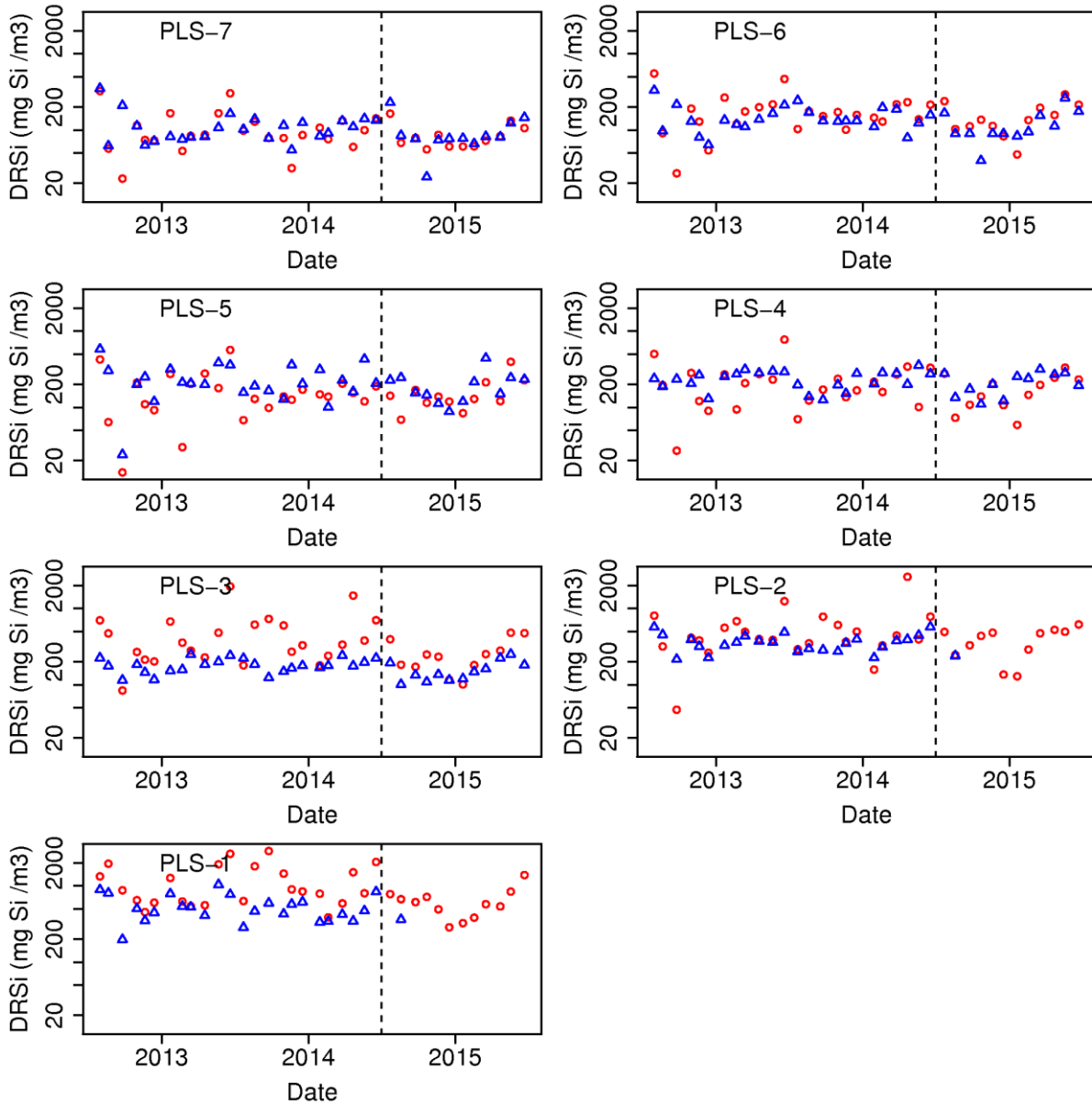
Dissolved organic phosphorus has been calculated by subtracting measured DRP concentrations from measured TDP concentrations. The inferred concentrations of dissolved organic phosphorus are usually low. Indeed, they are sometimes negative. In the real-world, negative concentrations are impossible. The negatives arise because of unavoidable sampling/measurement error (imprecision) associated with the measurements of DRP and TDP.



**Figure 4-11: Inferred near-surface (red) and near-bed (blue) dissolved organic phosphorus (TDP-DRP) at the seven Marlborough District Council Pelorus water quality sites.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

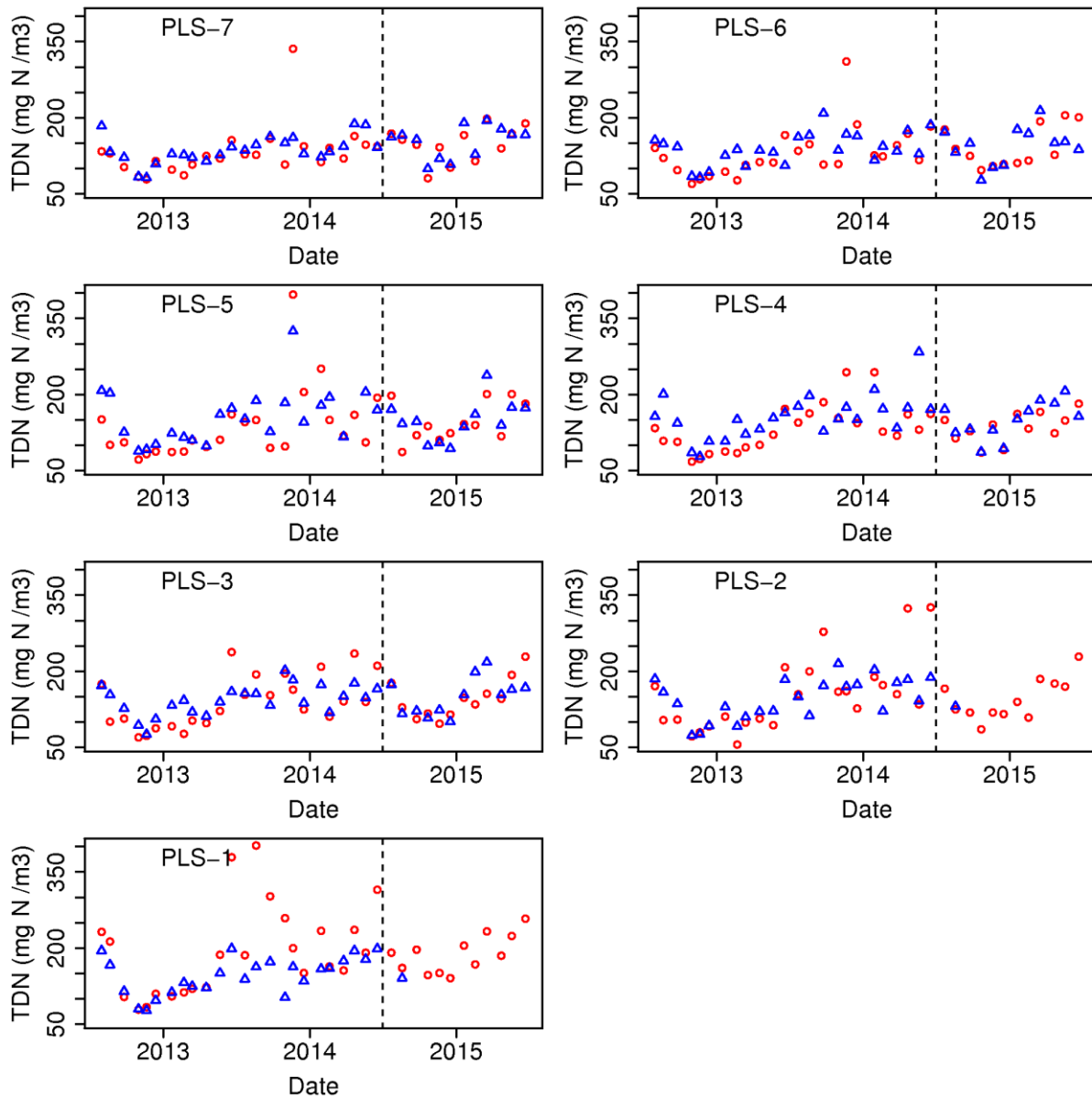


## 4.9 Dissolved reactive silicon



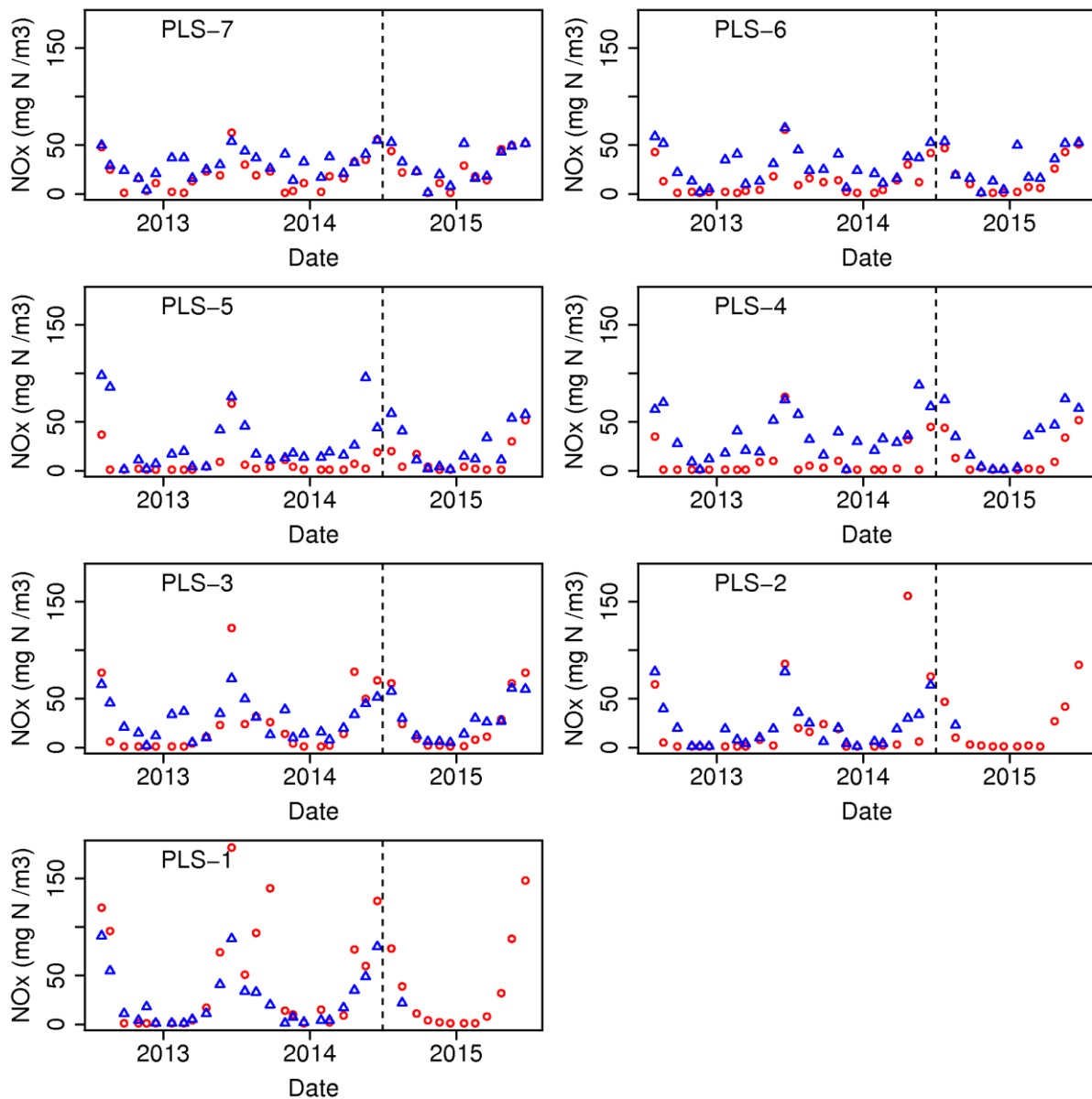
**Figure 4-12: Dissolved reactive silicon concentrations near-surface (red) and near-bed (blue) at the seven Marlborough District Council Pelorus water quality stations.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

## 4.10 Total dissolved nitrogen



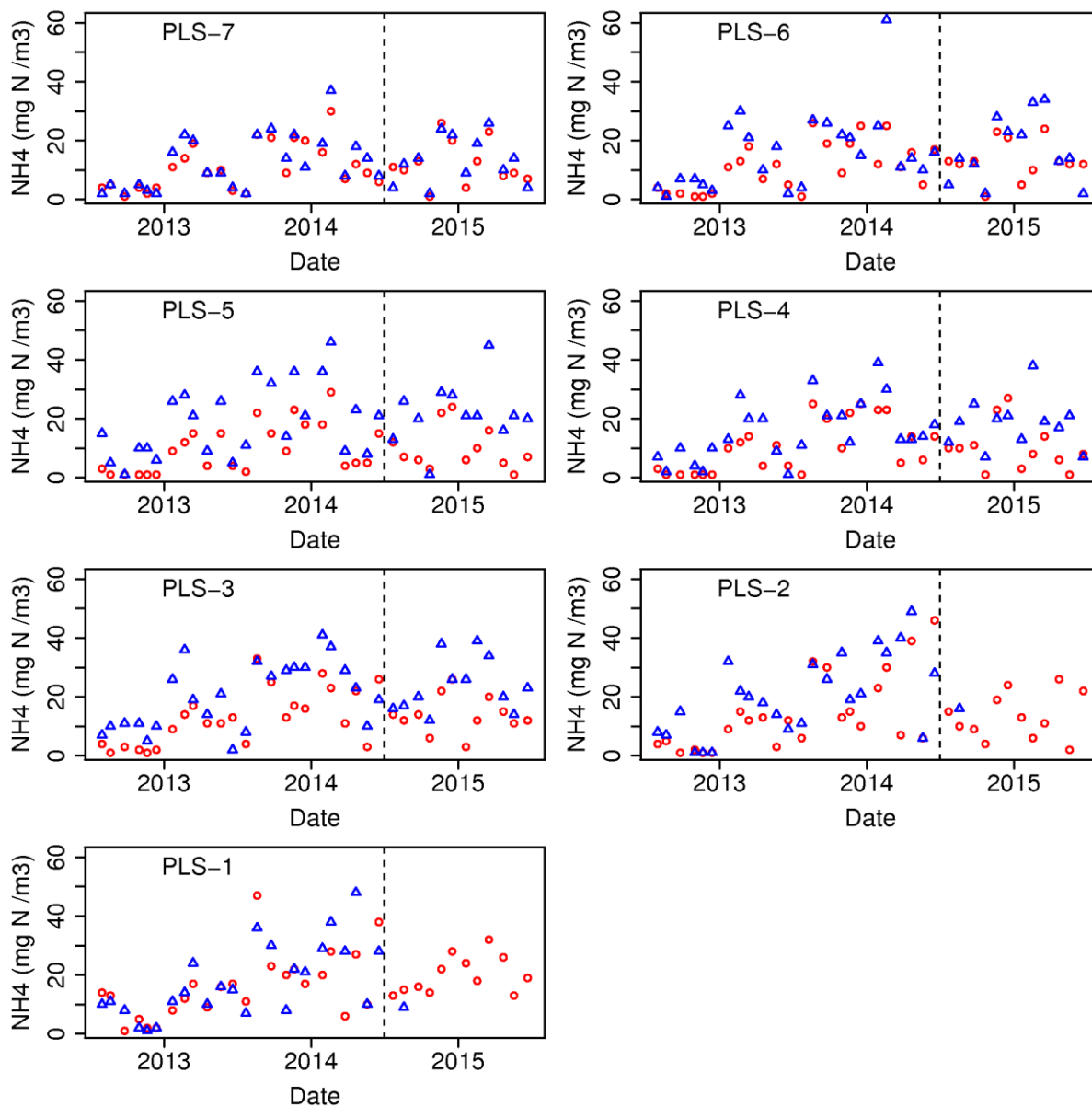
**Figure 4-13: Total dissolved nitrogen near-surface (red) and near-bed (blue) measured at the seven Marlborough District Council Pelorus water-quality stations.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

## 4.11 Nitrate



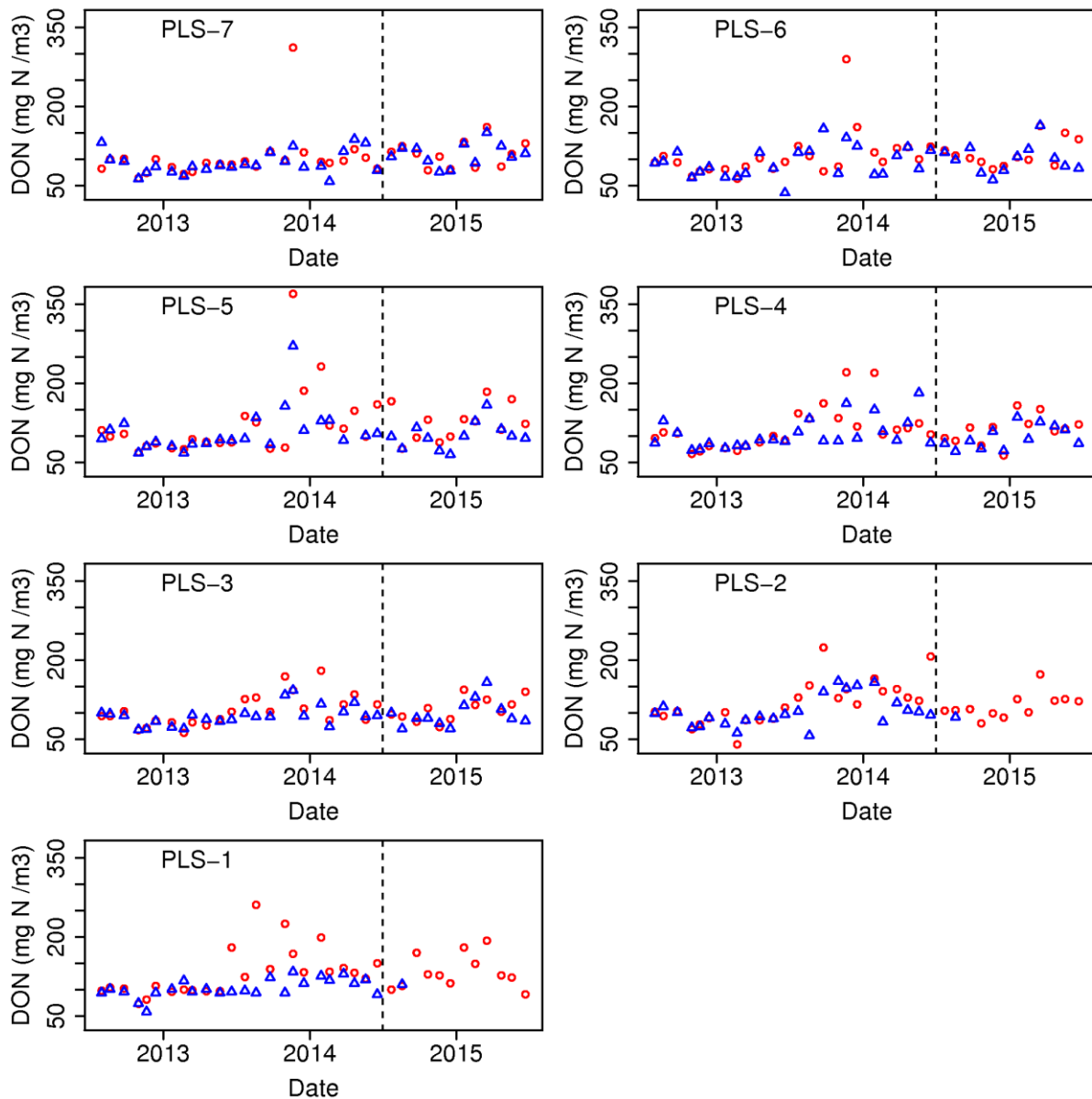
**Figure 4-14: Nitrate concentrations near-surface (red) and near-bed (blue) measured at the seven Marlborough District Council Pelorus water-quality stations.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

## 4.12 Ammoniacal nitrogen



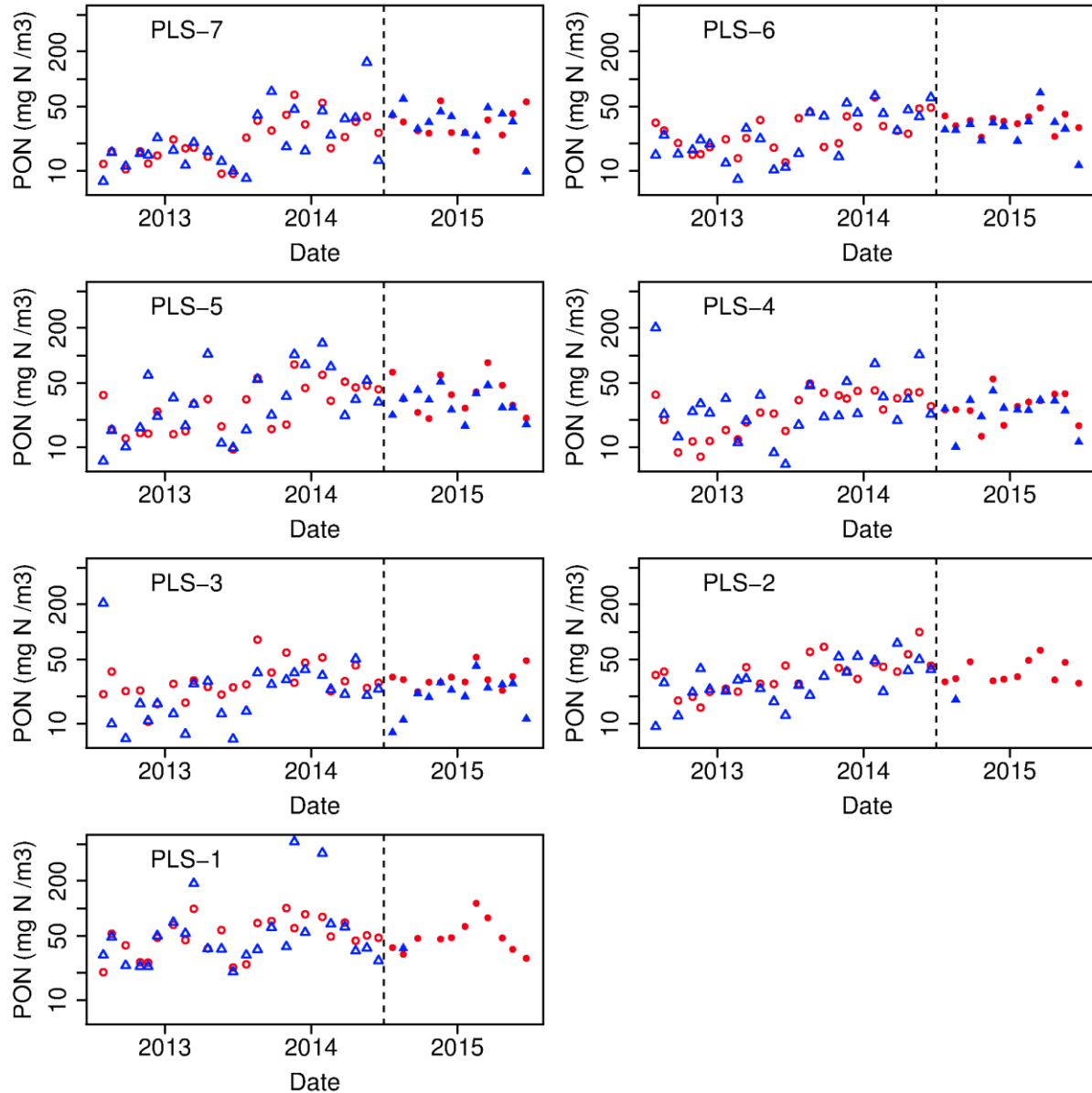
**Figure 4-15: Ammoniacal nitrogen near-surface (red) and near-bed (blue) measured at the seven Marlborough District Council Pelorus water-quality stations.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

## 4.13 Dissolved organic nitrogen



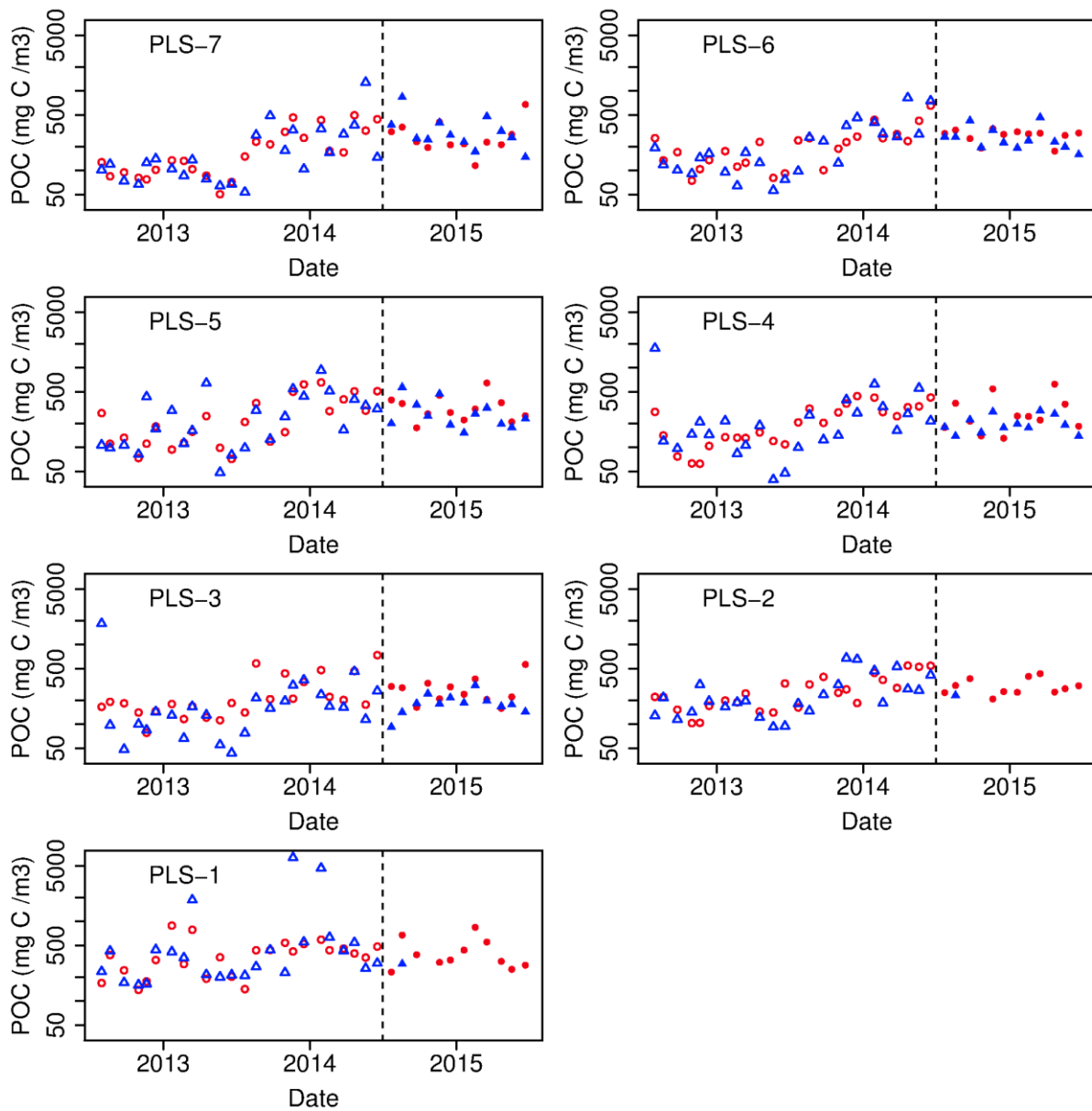
**Figure 4-16: Inferred dissolved organic nitrogen concentrations near-surface (red) and near-bed (blue) at the seven Marlborough District Council Pelorus stations.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

## 4.14 Particulate nitrogen



**Figure 4-17: Particulate nitrogen near-surface (red) and near-bed (blue) at the seven Marlborough District Council Pelorus monitoring stations.** The dashed vertical line (July 1, 2014) and switch from open to closed symbols separates measurements of Particulate Organic Nitrogen sampled at one metre depth using a Van Dorn bottle from measurements of Particulate Nitrogen measured sampled from the upper 15 using a hose-sampler.

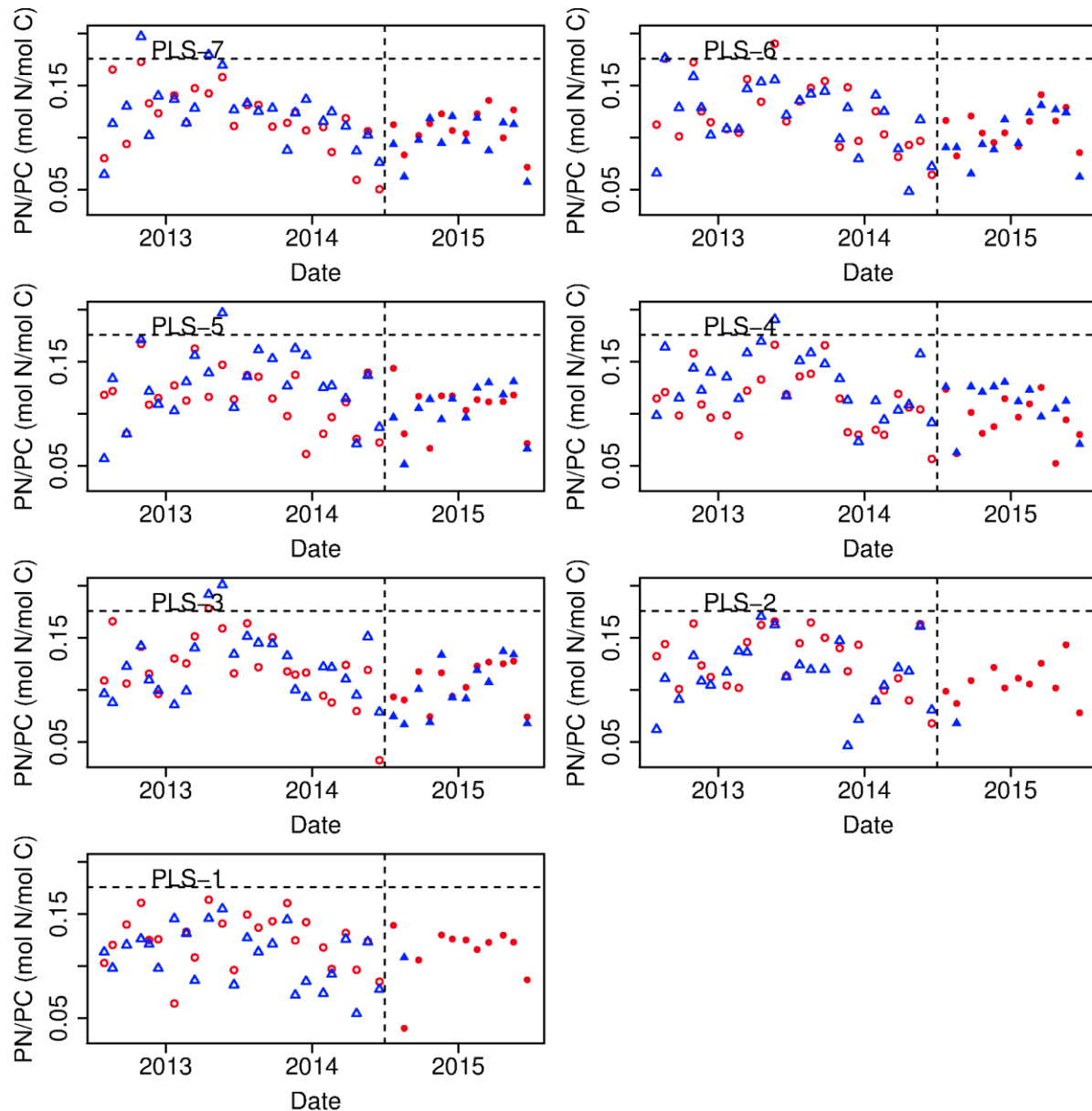
## 4.15 Particulate carbon



**Figure 4-18: Particulate carbon near-surface (red) and near-bed (blue) at the seven Marlborough District Council Pelorus monitoring stations.** The dashed vertical line (July 1, 2014) and switch from open to closed symbols separates measurements of Particulate Organic Carbon sampled at one metre depth using a Van Dorn bottle from measurements of Particulate Carbon measured sampled from the upper 15 using a hose-sampler.

## 4.16 PN:PC

In comparison with terrestrial particulate organic matter, fresh marine particulates (living plankton and freshly dead plankton) tends to have a high N:C content.

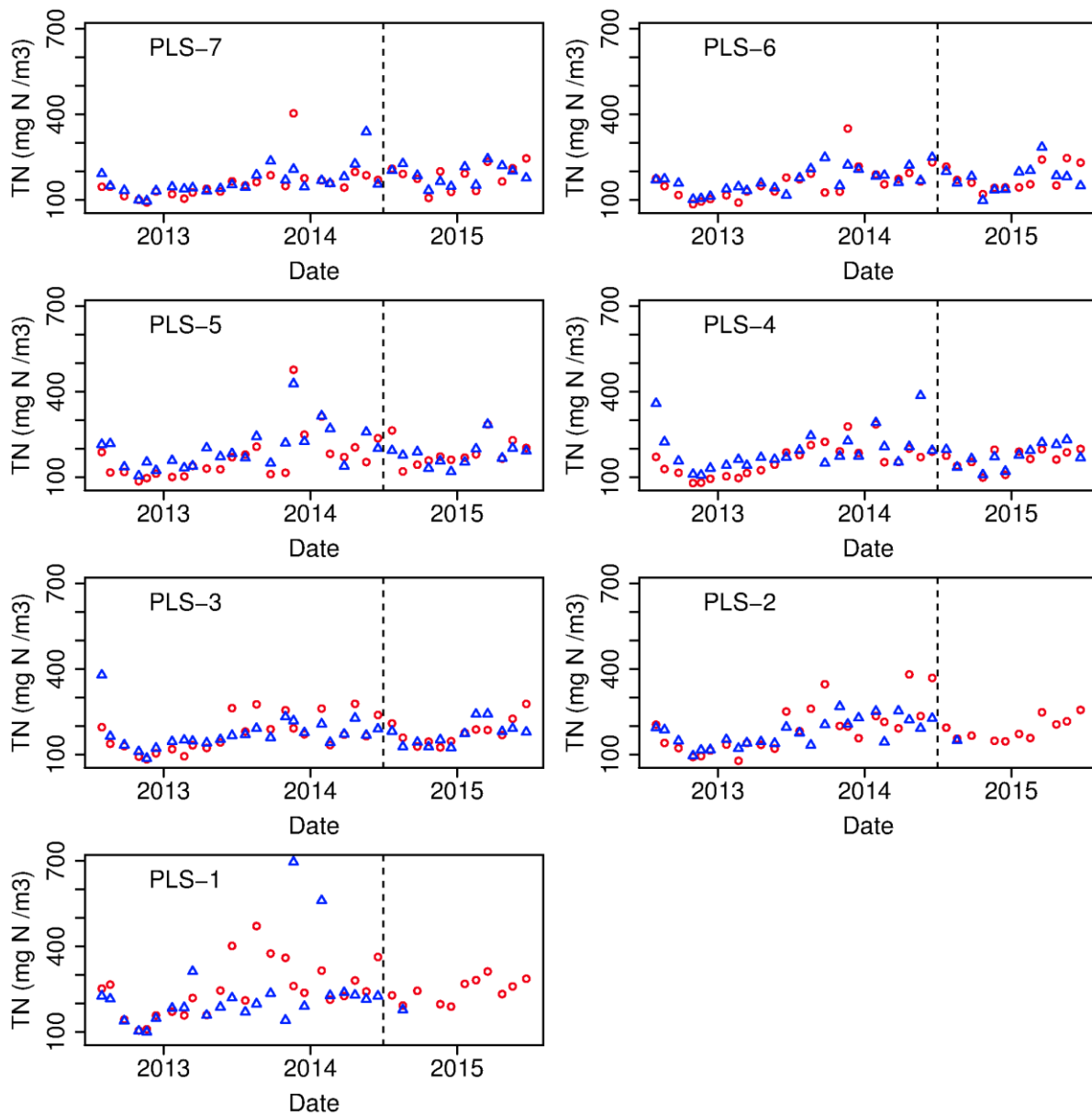


**Figure 4-19: PN:PC ratios in near-surface (red) and near-bed (blue) samples at the seven Marlborough District Council Pelorus sampling sites.** The vertical dashed line (1 July, 2014) and switch from open to closed symbols separates measurements of Particulate Organic Carbon sampled at one metre depth using a Van Dorn bottle from measurements of Particulate Carbon measured sampled from the upper 15 m using a hose-sampler. The horizontal dashed line represents the so-called 'Redfield ratio' (empirically determined N:C ratio for particulate material in oceanic waters).



## 4.17 Total nitrogen

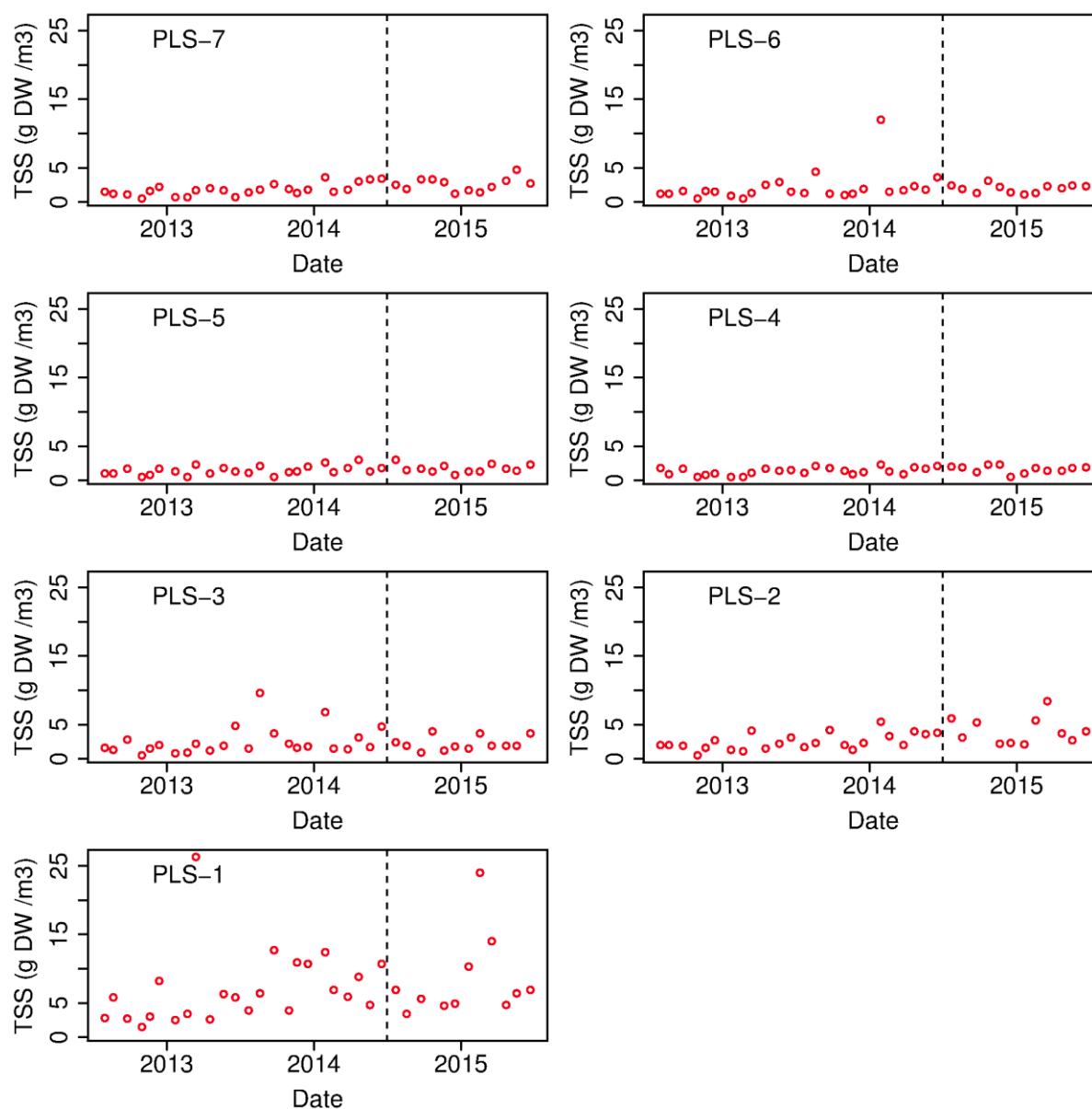
Total nitrogen is the sum of particulate and dissolved nitrogen components.



**Figure 4-20: Total nitrogen in near-surface (red) and near-bed (blue) water measured at the seven Marlborough District Council Pelorus sampling sites.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

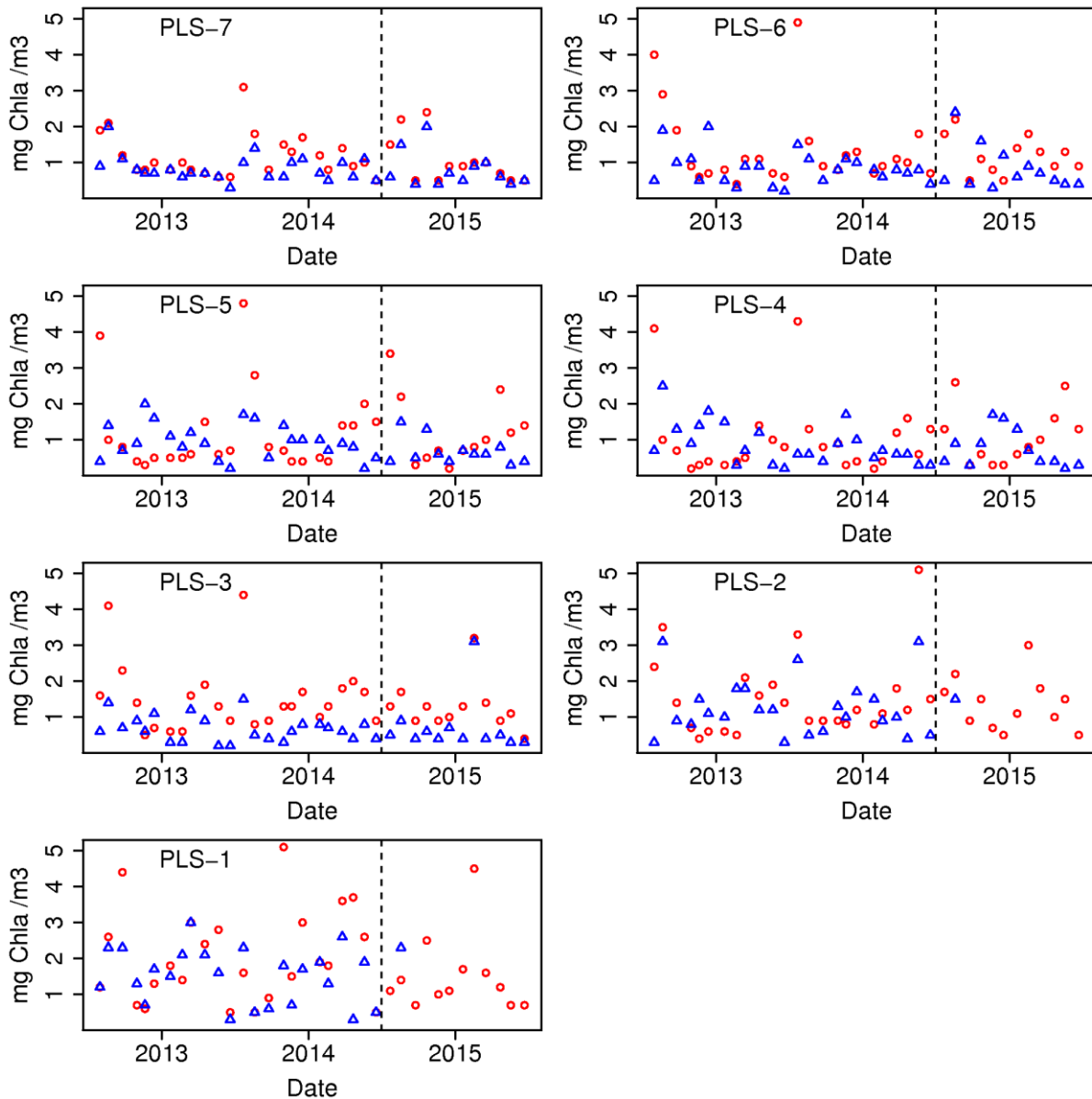
## 4.18 Volatile Suspended Solids

Whilst both carbon and nitrogen are components of volatile suspended solids, VSS concentration is measured independently of P(O)C and P(O)N. Thus, VSS provide an alternative/independent (to POC and PC) measure of the abundance of particulate organic matter.



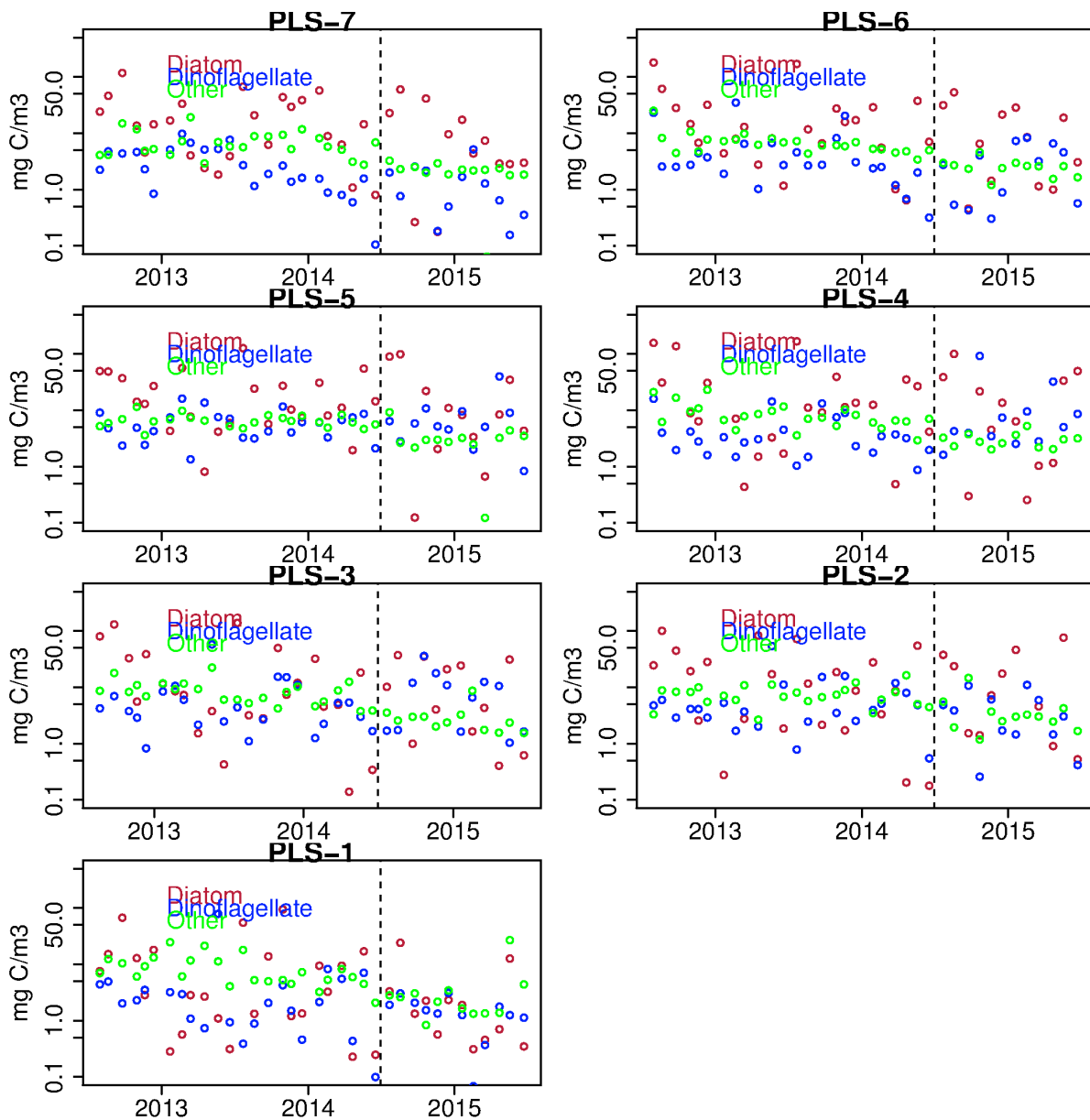
**Figure 4-21: Volatile suspended solids concentrations measured in the near-surface waters at the seven Marlborough District Council Pelorus sites.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

## 4.19 Chlorophyll



**Figure 4-22: Chlorophyll concentrations measured near-surface (red) and near-bed (blue) at the seven Marlborough District Council Pelorus stations.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

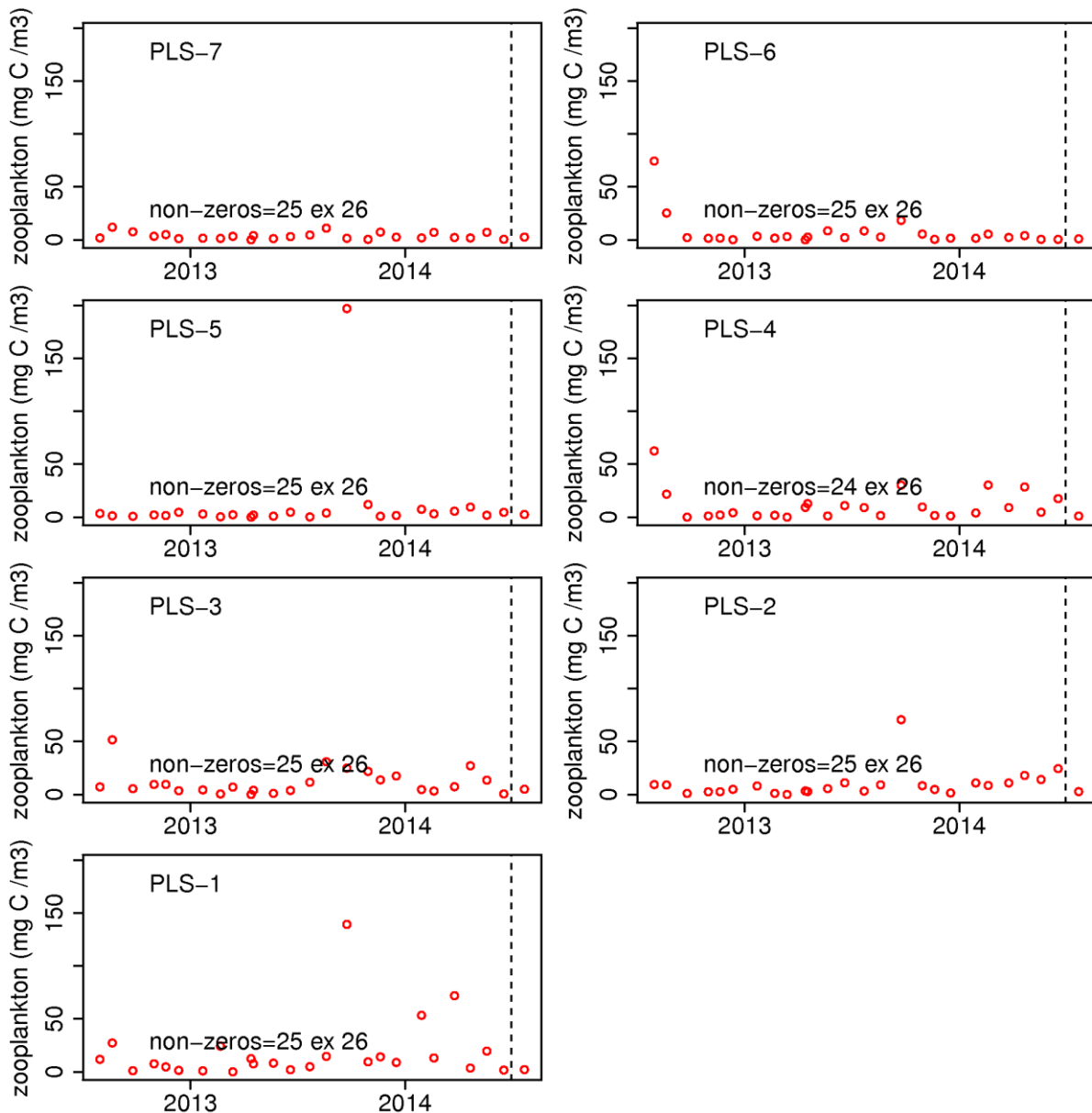
## 4.20 Algal carbon



**Figure 4-23: Phytoplankton carbon concentration from cell counts and cell dimensions at the seven Marlborough District Council Pelorus stations (near surface water samples).** Red symbols: diatoms; blue symbols: dinoflagellates; green symbols: other taxa. The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

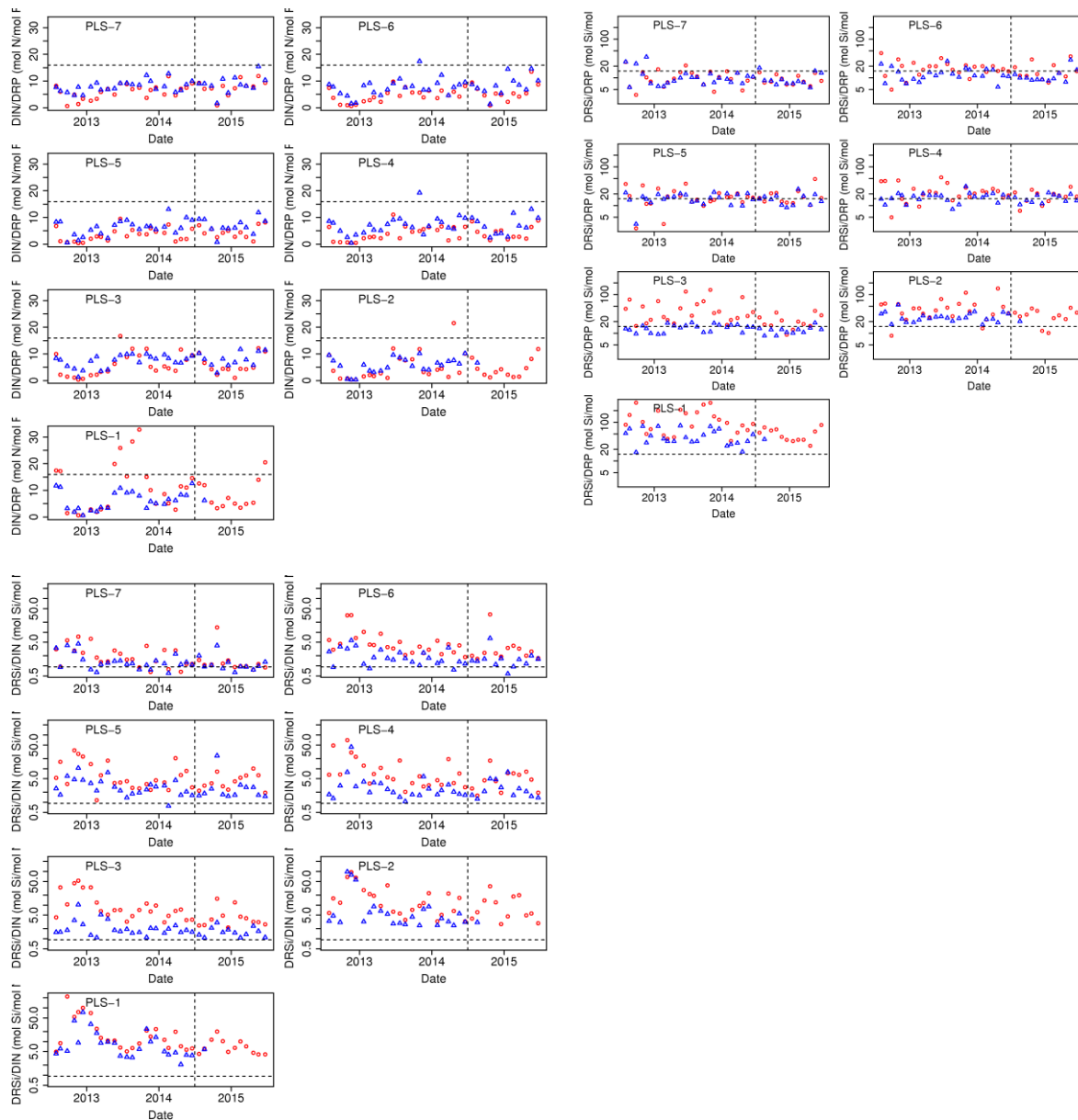
## 4.21 Zooplankton carbon

Zooplankton were counted only during two of the years. For metazoan (multi-cellular). Biomass estimates are from counts, and measurements of the dimensions of a few, representative individuals. The size range spanned by different individuals of any given taxa can be very large (dep. upon developmental stage). Thus, the biomass estimates are extremely imprecise (qualitative).



**Figure 4-24: Zooplankton biomass inferred from counts and dimensions at the seven Marlborough District Council Pelorus sites (near surface water samples).** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler.

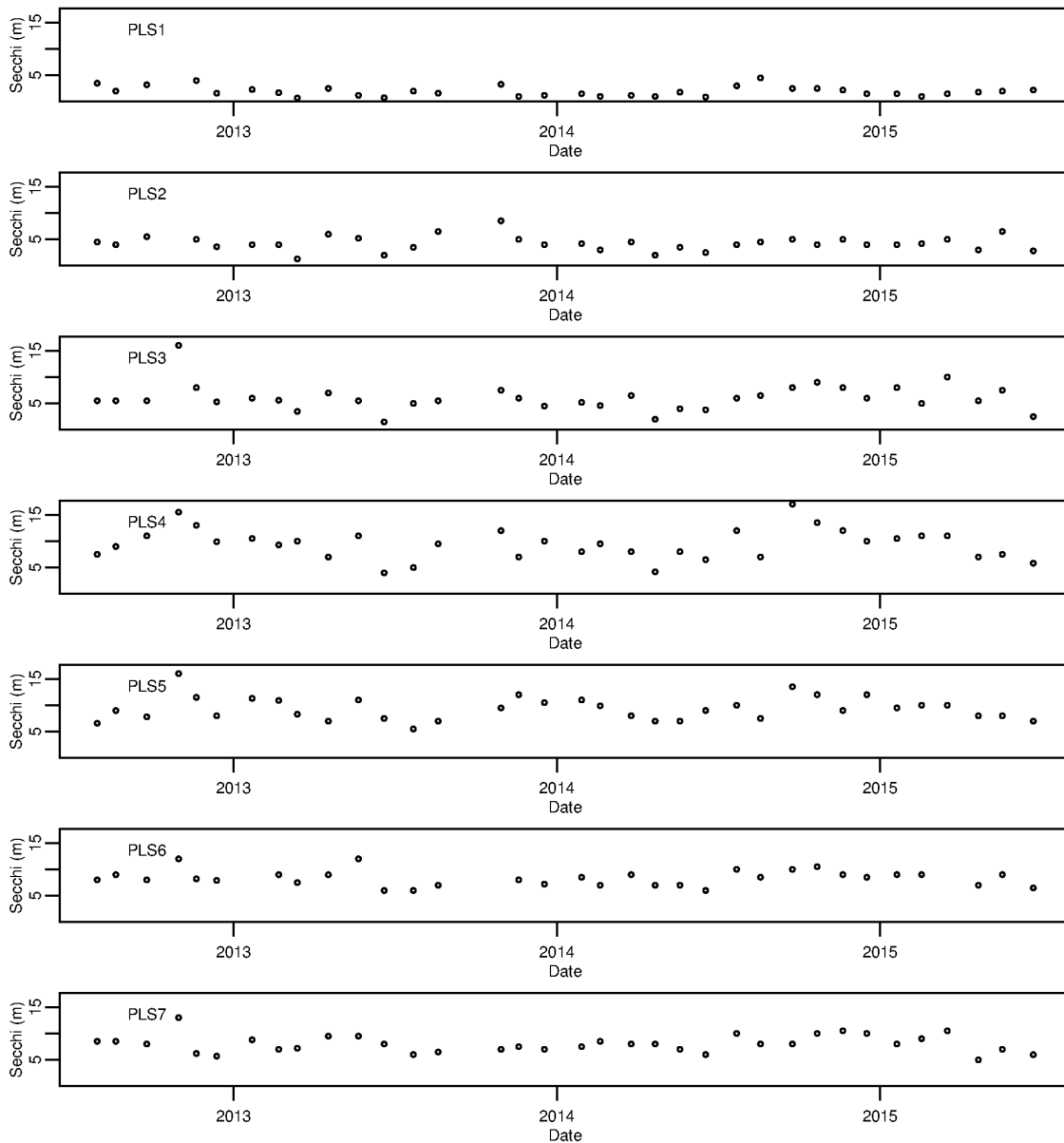
## 4.22 Elemental ratios



**Figure 4-25: Ratios of dissolved inorganic nutrients measured near-surface (red) and near-bed (blue) at each MDC Pelorus site.** The dashed vertical line (1 July 2014) separates data collected with a Van Dorn bottle at 1 m depth (to left of line) from data collected from the upper 15 m of the water column using a hose-sampler. The horizontal dashed line indicates the Redfield ratio for the pair of elements in question. When the symbols lie below the line, the element in the numerator of the quotient expressed in the y-variate is the more limiting of the two. If the symbols lie above the line, the element in the denominator of the quotient is the more limiting. Thus, DIN and DRSi are both almost invariably more limiting than DRP at all sites. DIN is almost invariably the most limiting nutrient. Note, that in the context of these plots, the limiting element is the one which would first become exhausted if growth were allowed to continue for sufficiently long (i.e., the elemental resource that will become exhausted first). This long-term limiting element may not be the resource (or even the element) which most limited/constrained the instantaneous growth of the algae at the sampling instant.

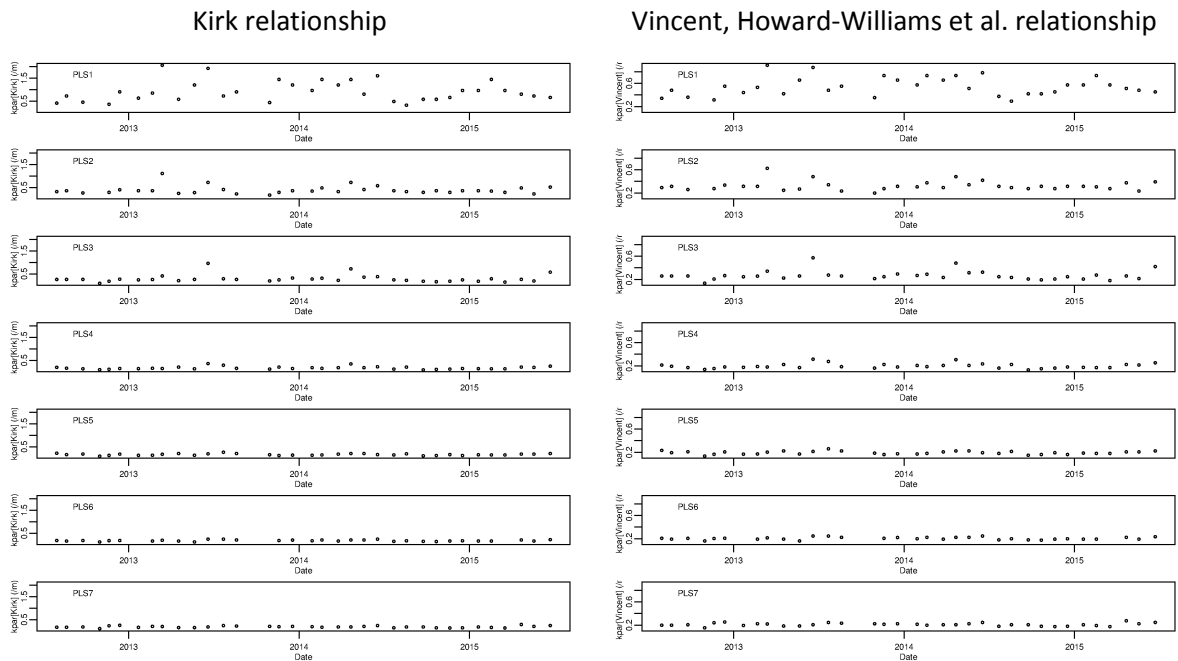
### 4.23 Secchi disk depth

Secchi disk depths range from circa 2-5 m (at the inner-most Pelorus sites) up to circa 5-15 m out central and outer sites.



**Figure 4-26: Secchi disk depth measured in Pelorus Sound at the seven Marlborough District Council stations.**

As noted above, measurements of Secchi disk depths provide a (often poor) proxy measure from which the PAR attenuation coefficient may be derived by exploiting empirical relationships. Kirk (1983) provides one such empirical relationship based upon international data. Vincent, Howard-Williams et al. (1989) provide data (from Pelorus Sound) that enable an alternative (perhaps more appropriate) relationship to be derived.



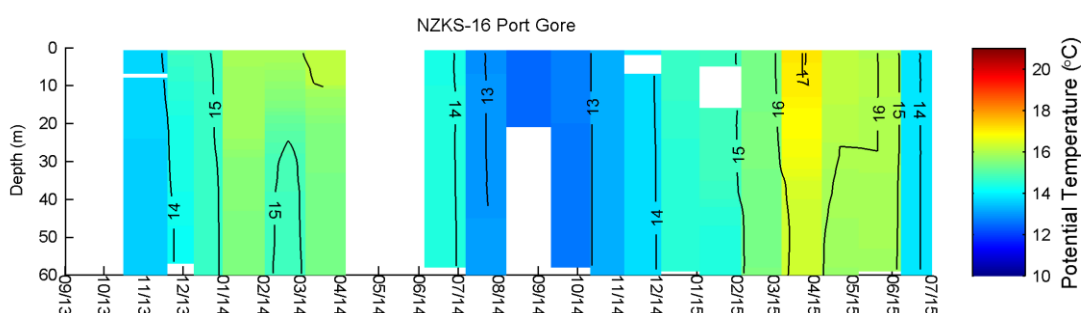
**Figure 4-27: PAR attenuation coefficients in Pelorus Sound inferred using the relationship described in Kirk (left panels) and the data of Vincent et al. (right panels).**



## 5 Results (Port Gore)

The Port Gore sampling location lies approximately half-way between the seaward ends of Cape Lambert and Cape Jackson (Figure 2-1). Port Gore has only a very small catchment and that is not subject to intensive farming or commercial forestry. The inner parts of Port Gore (Pig Bay and Melville Bay) do contain some mussel farms but we believe that the waters in the vicinity of the sampling location will usually be pristine (or nearly so) – and probably have water-quality properties that are very similar to those of Cook Strait.

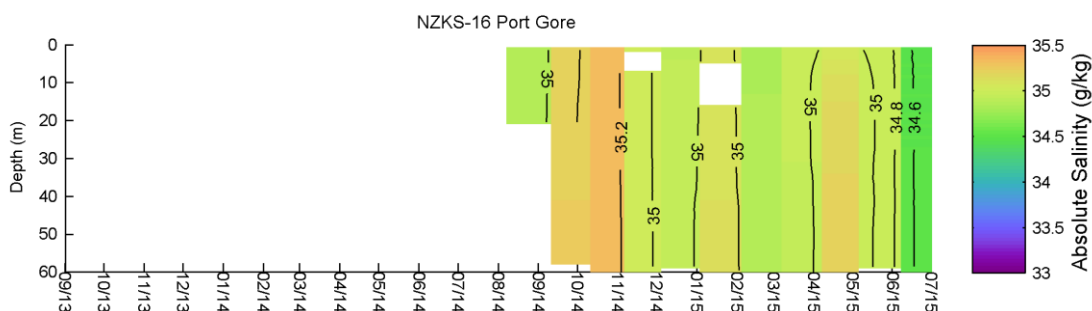
### 5.1 CTD temperature profiles



**Figure 5-1: Contour plots of the evolving depth profiles of temperature through time at the Cook Strait mouth of Port Gore.** Data are from the monthly CTD casts. White space indicates missing/rejected data (or the maximum depth to which the cast extended).

Temperature profiles recorded since Nov 2013 show temperature ranging between ~12.5 to 17°C. The 2015 summer resulted in higher temperatures than those recorded in 2014. The water column is usually well mixed, with some evidence of stratification between Feb-May 2015. However the small temperature gradients and minimal vertical differences in salinity (see below) indicate that this stratification was weak.

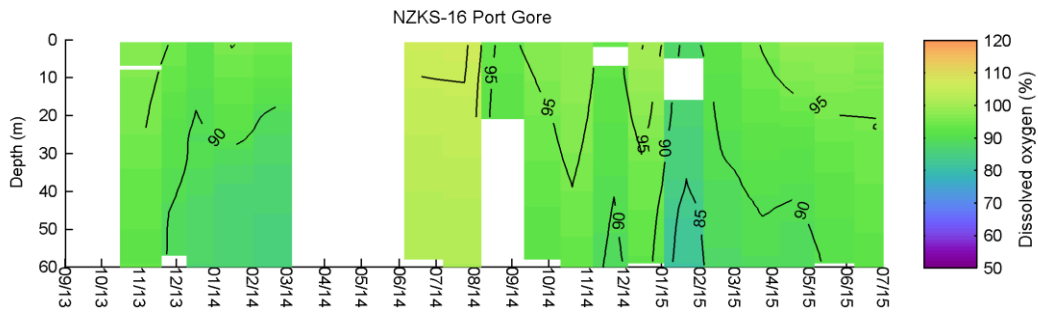
### 5.2 CTD salinity profiles



**Figure 5-2: Contour plots of evolving depth profiles of salinity through time at the Cook Strait mouth of Port Gore.** Data are from the monthly CTD casts. White space indicates missing/rejected data (or the maximum depth to which the cast extended).

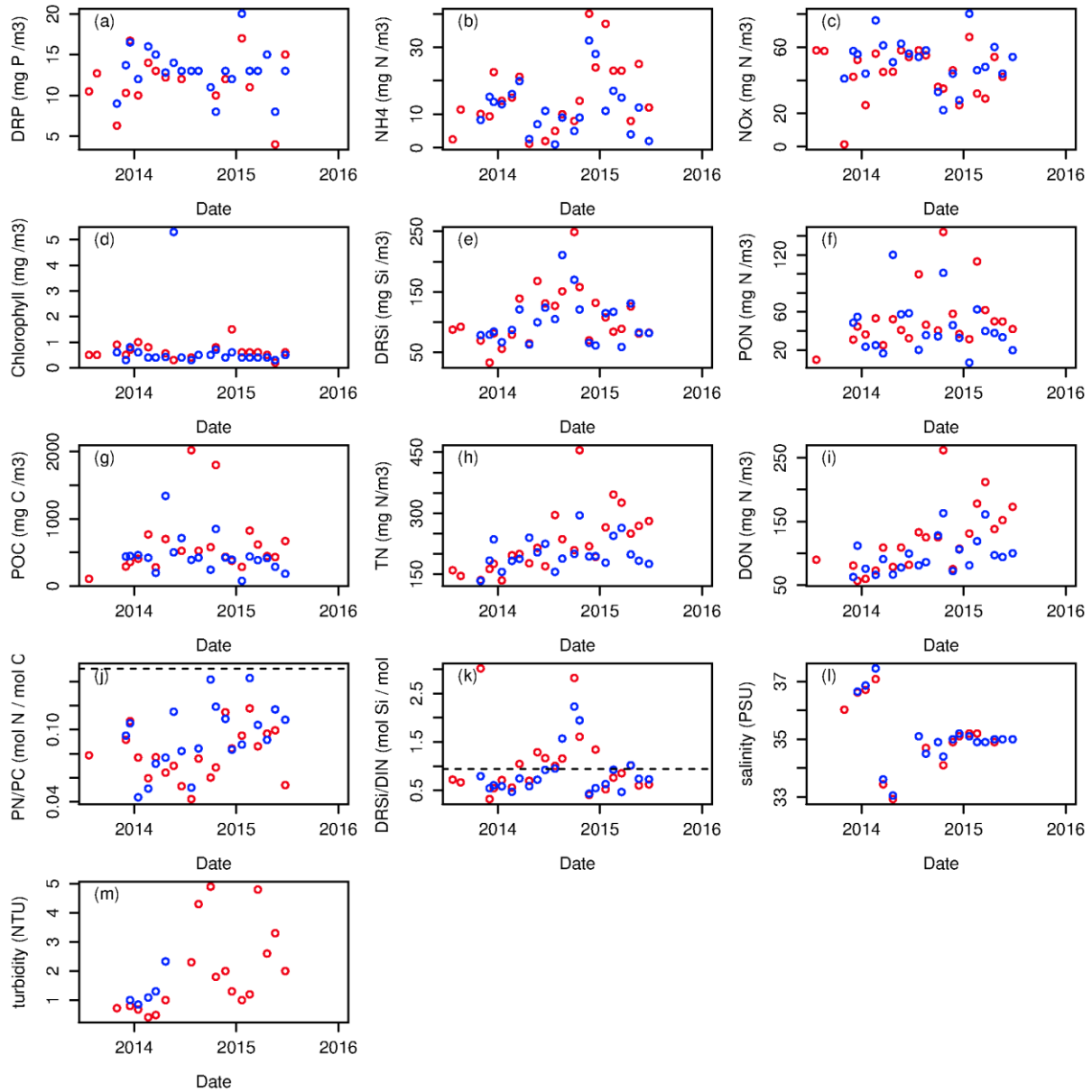
Salinity data from Sept 2014 to June 2015 are shown. While there is some variation over time, there is very little vertical difference in salinity. Data prior to Sept 2014 are not shown due to a poorly functioning conductivity sensor.

### 5.3 CTD oxygen profiles



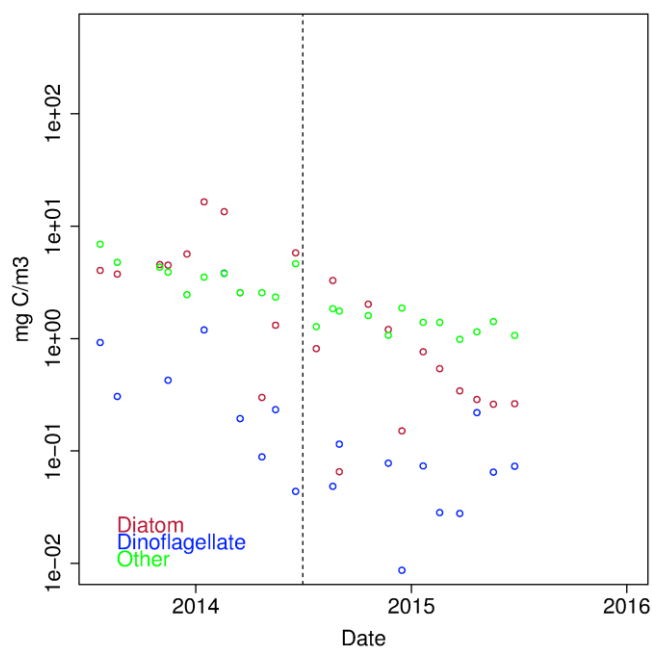
**Figure 5-3: Contour plots of evolving depth profiles of dissolved oxygen through time at the Cook Strait Mouth of Port Gore.** Data are from the monthly CTD casts. White space indicates missing/rejected data (or the maximum depth to which the cast extended).

## 5.4 Other water quality characteristics



**Figure 5-4: Water quality characteristics measured at the Cook Strait mouth of Port Gore from the New Zealand King Salmon Ltd, Marlborough District Council and NIWA sampling programmes.** Red symbols denote near-surface data (hose sample to approx. 15 m); blue symbols denote deep-water data (Van Dorn sampler at approx. 60 m – being circa 2 m above the bed). The salinity data stemming from the NZKS sampling are from the CTD cast rather than laboratory analyses of water samples returned to the laboratory. They regarded as suspect (see section 2.2).

## 5.5 Algal carbon



**Figure 5-5: Time-series of taxon-specific, near-surface phytoplankton biomass concentration measured at the Port Gore station in the NZKS, MDC and NIWA time-series.** Red symbols indicate diatom carbon concentration, blue symbols indicate dinoflagellate carbon concentration and green symbols indicate the total carbon concentration of 'other phytoplankton taxa' (which are mainly small flagellates).

## 6 Data exclusions and other matters

**Table 6-1: Summary of sampling records which are considered dubious and of records which have been rejected.**

Site	Date	Quantities	Comment 1	Comment 2
QCS-4 (surface)	2012-05-21	POC & PON	Lab comments: sample mix -up therefore 2 possible results for QCS-4. PON:4.9 or 23 POC: 45.8 or 131	4.9 and 45.8 are plotted
QCS-5 (surface)	2012-05-21	POC & PON	Lab comments: sample mix -up therefore 2 possible results for QCS-5. PON:19.8 or 10.3 POC: 131 or 40.4	19.8 and 131 are plotted
QCS-4 (surface)	2012-08-20	POC & PON	No results from lab analyser. Suspicion is that the sample from QCS-4 (surface) did not drop into the analyser until the subsequent (QCS-5 (surface) sample was loaded.	See below

Site	Date	Quantities	Comment 1	Comment 2
QCS-5 (surface)	2012-08-20	POC & PON	See above. The values recorded for QCS-5 <u>may</u> be falsely high (due to possibly summing the masses stemming from QCS-4 and QCS-5 samples)	Data have, nonetheless, been retained and plotted in Figure 3-17 and Figure 3-18. Inspection of those figures indicates that the near-surface PON and POC concentrations (seemingly) recorded for QCS-5 on this date were high in comparison with those on the preceding and succeeding sampling occasions
QCS-1 (surface)	2013-03-21	POC	Originally recorded as 15.9, but this was suspiciously low. Laboratory confirmed a transcription error.	Amended value (230) inserted on 2015-04-02
QCS-2 (deep)	2014-11-23	PC	Initial PC read was very, very high (2440) rel to PN, or chl in surface water sample. Indeed, very high rel to PC measured anywhere/anytime in QCS.	We reran the sample and got 245. This is consistent with other data and has been adopted.
PLS-2 (surface)	2013-11-20	POC & PON	Recorded as 419 and 61 respectively. Those appeared unusually high. Thus, the samples were reanalysed.	Reanalysis (of the little material that remained) yielded 520 & 54.5 – suggesting that POC and PON were indeed unusually high on this occasion

Site	Date	Quantities	Comment 1	Comment 2
PLS-1 (surface)	2014-01-29	POC & PON	Recorded as 589 and 81.1 respectively. Those appeared unusually high. Thus, the samples were reanalysed.	Reanalysis (of the little material that remained) yielded 504 & 42.1 – suggesting that POC and PON were indeed unusually high in this sample (but see below)
PLS-1 (deep)	2014-01-29	POC & PON	Exceptionally high POC (4660) & PON (402). Dr Steve Urlich (MDC) states that the water at PLS-1 was unusually turbid, but also that the sample was taken in a hurry such that Van Dorn sampler may have hit the seabed and stirred material up.	See above: near-surface sample also contained high particulate concentrations.
PLS-1 (deep)	2014-03-26	salinity	Unusually low (29.5) but the sample was re-measured and same value was returned. Assume genuine.	
PLS-2 (deep)	2014-03-26	salinity	Beaker leaked. Insufficient water to measure salinity.	
PLS-5 (deep)	2014-04-22	TDN	Originally recorded as 999 – which is exceptionally high (esp as NH <sub>4</sub> and NO <sub>3</sub> were unremarkable). Lab manager suspects sample was contaminated during filtration.	Value of 999 rejected. Treat as a missing value

Site	Date	Quantities	Comment 1	Comment 2
PLS-1 (depth-averaged)	2014-10-22	Turbidity (106), SS (234), VSS (2.5), SIS (48.7), PC (4130) and PN (331).	All anomalously high. Dr Steve Urlich (MDC) states that the tube-sampler hit the seabed and probably sucked up resuspended material.	Data rejected. Treat as missing values. Solute concentrations were unexceptional and have been retained.
PLS-2 (depth averaged)	2014-10-22	Turbidity (33.1), SS (51.2), VSS (12.4), SIS (222), PC (968) and PN (93.2).	All anomalously high. Dr. Steve Urlich (MDC) states that the tube-sampler hit the seabed and probably sucked up resuspended material.	Data rejected. Treat as missing values. Solute concentrations were unexceptional and have been retained.
Port Gore (deep)	2014-05-22	Chlorophyll concentration	Recorded as 5.3 mg m <sup>-3</sup> . This is far higher than all other chlorophyll concentrations (deep-water or near-surface) that have been measured at this site. Indeed, the highest deep-water chlorophyll concentration measured anywhere in the Sounds.	Values approaching 5 mg m <sup>-3</sup> have been recorded in some Queen Charlotte deep-water samples and values in excess of 5 mg m <sup>-3</sup> have been recorded in near-surface samples from Pelorus and Queen Charlotte. There was too little water to permit a reanalysis, but the lab has checked that the value was not a transcription error. Chlorophyll samples are difficult to contaminate. We are suspicious of this value, but we let it stand for the present.



Site	Date	Quantities	Comment 1	Comment 2
QCS-1 CTD	2015-06-25	Temperature, salinity, density, oxygen	Large step increase in temperature seen at 18m depth resulting in decrease in salinity and density. Similar step decrease in dissolved oxygen. Cause unknown, but rapid descent rate was recorded and default averaging (4 second) was engaged	Data rejected. Treat as missing values. Recommend slower descent rate (<1m/s) and ensure the default averaging is turned off.
QCS CTD	24/7/2014	Conductivity, salinity, density	Conductivity values appear too low, affecting salinity and density	Data rejected.

## 7 Conclusions & Recommendations

### 7.1 Data distributions and Flag values

Appendix B and Appendix C present histograms which illustrate the empirical probability distributions of the values associated with each water-quality variable measured in Queen Charlotte Sound/Tory Channel (Appendix B) and Pelorus Sound (Appendix C). The text within each probability density function plot lists the quantity-values (usually, concentrations) corresponding the 50<sup>th</sup>, (median), 95<sup>th</sup>, 98<sup>th</sup> and 100 percentile.). Data that Table 6-1 listed as having been excluded were also excluded when calculating these probability density functions. The data have been divided into sub-categories by Sound, season (quarter of year) and depth-band (near-surface versus near-bed).

The density functions will not be discussed in detail since they are merely a different way of summarising the raw data presented in the time-series plots of sections 3 and 4. The percentile distributions can be used to apply a degree of quality control to incoming data (from newly collected samples). For example, one could set upper (and lower) threshold values that incoming data might reasonably be expected to fall within. Should an incoming data item fall outside the specified band, it could be subject to greater-than-normal scrutiny before being accepted (or rejected). For example, should a TSS concentration be unusually high, one might ask questions such as:

- Did the sampler hit the seabed such that sediments could have been stirred up (temporarily raising the concentration of suspended sediments)?
- Were other presumed correlates of suspended sediments (SIS, VSS, PC, PN) also unusually high?
- Do the boat crew report that the water did, indeed, appear unusually turbid?
- Had there been a recent river-flood that may have introduced sediment?

Depending upon the answers to questions such as these, the data-administrator would make a call as to whether to: (a) definitively accept the data or (b) definitively reject it.

Choosing the upper and lower threshold values would be a subjective decision but inspection of the probability density functions suggests:

- For some variables (e.g., DRP), the quantity-values (usually, concentrations) associated with the 95%, 98% and 100%iles differ by only relatively small increments. This tends to imply that values which are dramatically larger than the maximum historical value are unlikely to arise in the future – unless there is an ongoing upward trend in the variable.
- For other variables (e.g., TSS, turbidity, NH<sub>4</sub>-N), the increments between the 95%, 98% and 100%iles are relatively larger. Nonetheless, in the majority of even these cases, the cumulative density function (the asymptotic ‘curve’) has converged close to 1.0 before the 95<sup>th</sup> percentile. This pattern tends to imply that, whilst future values are unlikely to surpass the historical maximum (unless there is an upward trend with respect to time), those which do exceed the historical maximum may do so by a large margin.

- For some variables (e.g., NO<sub>3</sub>-N), the various percentiles change markedly with season and/or depth. For others, there is little seasonal variation (e.g., near-surface turbidity in Queen Charlotte/Tory).

Choosing ‘guard values’ is a subjective exercise. If the upper thresholds are set too low, many incoming data will be flagged as deserving additional scrutiny, but subsequently accepted. Conversely, if the upper threshold is set too high, some ‘bad’ data may slip through without attracting due scrutiny. If guard values are to be based upon the historical data presented in this document one should note:

- Some extreme historical data were excluded before the time-series plots and percentile distributions were made. Thus, the data which we present are only those observations we believe are plausible rather than the all of observations. Our judgement of plausibility was based on an informal identification of extreme values followed by inquiries as to what might have driven them (e.g., bias arising because sampling device hit the bottom (reject the data) versus a natural extreme associated with sampling after a river flood (retain the data)).

It is our opinion that:

- guard-values should not be used as the sole means by which to definitively accept or reject incoming data; rather, they should be used to flag data that deserve additional scrutiny
- guard values should be re-evaluated from time-to-time (lest there be long-term water-quality trends)
- data which are rejected, should nonetheless, be recorded elsewhere (so that the data can be re-incorporated in the event subsequent information leads to a change in the criteria used to adjudicate upon ‘unusual data’.

## 7.2 Dissolved oxygen and NZKS management protocols

New Zealand King Salmon Ltd and Marlborough District Council have agreed to a set of provisional standards to govern farm operations (Morrisey, Anderson et al. 2015). These include rules which state “... at sampling sites within 250 m of the net pens (i.e., Site 1 at Richmond, Site 8 at Waitata and Site 18 at Ngamahau), DO levels should not drop below 70% and at all remaining sampling sites, levels at all depths should not drop below 90% for any consecutive 3 months”. Inspection of the oxygen saturation profiles from the CTD casts (Figure 3-6, Figure 4-6) suggest that the oxygen saturations below 90% threshold have been a moderately frequent occurrence at some locations in both the Queen Charlotte/Tory and Pelorus systems (distant from fish farms). Usually, the lowest dissolved oxygen concentrations are found close to the seabed. These levels likely arise from a combination of benthic oxygen demand and stratification which limits delivery of near-surface waters to the seabed (surface waters are usually oxygen-rich due to photosynthesis and atmospheric exchange). We note: (a) the 70% threshold stems from a ‘close to farm’ threshold that is specified within the *Salmon Aquaculture Dialogue: Final standards for responsible salmon aquaculture* (SalmonAquacultureDialogue 2012)<sup>8</sup>. That document requires that oxygen be measured only at 5 m

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<sup>8</sup> Specifically, the Salmon Aquaculture Dialogue guidelines suggest that the at-farm weekly average dissolved oxygen saturation levels at 5 m depth should not fall below 70% unless the saturation levels at a reference site are also falling below 70% – in which case those at the farm should not be lower than those of the reference site. Literature suggests that, even amongst taxa that require relative high oxygen concentrations, few species would experience more than mild stress until oxygen saturations fell below circa 60% Vaquer-Sunyer, R.,

below the surface. In particular, it does not stipulate any oxygen saturation thresholds for far-field water and does not require that near-bed waters maintain oxygen concentrations above 70% (let alone 90%). The provisional MDC/NZKS standards are, therefore, much more stringent than those proposed in the salmon aquaculture dialogue. In the light of the MDC CTD-cast data, it seems likely that the threshold ‘*should not drop below 90% for any consecutive 3 months*’ (beyond 250 m from any farm) threshold is likely to be violated. Such a violation will trigger an assessment of whether the violation can be attributed to the new farms (Ngamahau, Richmond, Waitata). An intervention will be required only if they are deemed to be the cause of the breach.

### 7.3 Revisions to sampling patterns

#### 7.4 Tory Channel

The CTD and water-quality data from the water-quality station within Tory channel (QCS-3) indicate that the water is invariably well mixed (temperatures, salinities, and concentrations of nutrients and particulate are similar near-bed and near-surface). If a (relatively small) reduction in the cost of the sampling program is desirable, one might consider dropping either the near-surface, or the near-bed water-quality samples.

Even if costs are not an issue, one might consider dropping one of the two depth strata in favour of establishing an additional sampling station elsewhere within Tory/Queen Charlotte. More specifically, there have been anecdotal reports of environmental problems in the East Bay/Otanerau Bay region. Biophysical modelling suggests that East Bay/Otanerau/Onauku Bay may be relatively isolated from the main stem of Queen Charlotte (Hadfield, Broekhuizen et al. 2014). One might consider establishing a station in that region (perhaps, only a CTD station to complement the one in Endeavour Inlet).

If an additional station were to be established, one would need to give careful thought to the implications this would have for the agreement between NZKS/MDC concerning the management of NZKS fish farms (Morrisey, Anderson et al. 2015). The ‘rules’ within the agreement were based around the existing pattern of sampling (and NZKS monitoring data). Given the way that some ‘rules’ are phrased, adding any additional sampling stations into the network has the potential to increase the likelihood of an ‘exceedance’ being flagged (even if the environmental conditions at the pre-existing stations do not indicate any change in the frequency of exceedances).

#### 7.5 Handheld temperature, salinity and dissolved oxygen data

The near-surface data (temperature, salinity and dissolved oxygen) stemming from the measurements made at sea with hand-held devices duplicate measurements that are available from the CTD data (and, in the case of salinity, from subsequent measurements of the water-samples which are returned to the laboratory). There have been occasional problems with the CTD data. Similarly, there have been occasional problems with the hand-held data. Having two, independent data-sets provides a valuable means of cross-validation and ‘sampling-backup’. On the other hand, I assume that it implies a cost burden (increased time at sea, and increased time and resources spent processing and archiving two data-streams). Council might consider ceasing the measurement of near-surface salinity, temperature and dissolved oxygen with the hand-held devices.

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## 7.6 CTD profiling

To ensure reliable data are obtained from the CTD profiling, our experience shows that it is important to conduct frequent calibration checks on the sensors. Temperature sensors are generally fairly stable. The conductivity sensors on the Seabird instruments, in our experience, are remarkably stable over time. However, those used on the Exosonde have been more problematic. We recommend frequent checks of the conductivity sensor using standard solutions (or solutions with a known salinity). Until confidence about the reliability of the sensor is obtained, we suggest a calibration check of the C-T (conductivity and temperature) sensor prior to each deployment.

It is also preferable to use the same instrument, or when changing instruments to run a comparison between them to ensure data are comparable. If both instruments are calibrated properly then the data should be consistent, however there may be differences in sensor sensitivity that can be identified by a comparison.

The YSI Exosondes ship with a default 20-30 point moving average filter applied to the data (conductivity, temperature etc., but not pressure (depth)) collected by the sensors. At a sampling frequency of 4Hz, this means data stored is an average of data collected over the previous 5-7.5 sec. Consequently, inferred vertical profiles are severely affected unless this averaging is turned off. The averaging mode should be set to custom with the lowest possible averaging applied. Any filtering or averaging can be applied in post-processing (we typically bin the data, averaging all data collected within 1m intervals).

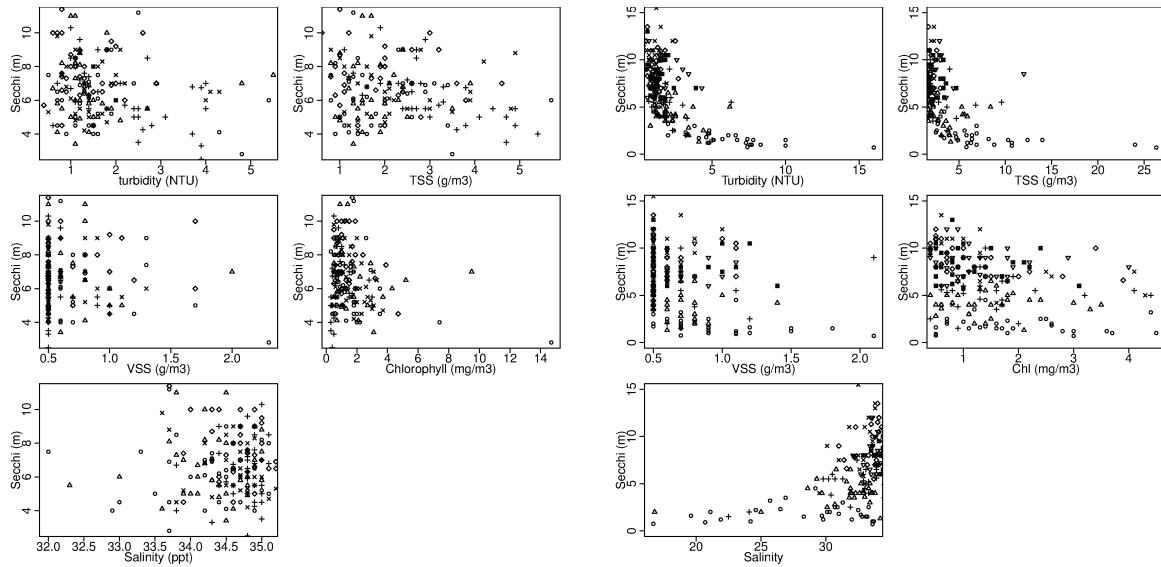
When taking the profile, it is important to hold the instrument just below the surface for approximately 1 min to let the temperature of the instrument equilibrate. The descent rate should be < 1m/s. This enables finer resolution (measurements at ~0.25m intervals). Sensors on the Exosonde have relatively slow responses making it even more important to lower the instrument slowly. The response time of various sensors on the Exosonde (according to the manual) are listed below. T63 is the time taken for the sensor to reach 63% of the final stimulus value when a step change is applied.

Sensor	Response time T63 (sec)
Conductivity	<2
Temperature	<1
Pressure	<2
Dissolved oxygen	<5
Chlorophyll, BGA-PC/BGA-PE	<2
Turbidity	<2

## 7.7 Secchi Disk

Secchi disk measurements have been made because (a) such data are intuitively appealing to a lay-public, (b) Secchi disk measurements are widely used around the world, so provide a means of inter-comparison, (c) as a potential 'backup' proxy for more fundamental properties such as suspended sediment or chlorophyll concentrations (lest the water-samples were spilt prior to lab. analysis), (d) as a potential proxy for direct measurements of the PAR attenuation coefficient.

In practice, whilst Secchi disk depth has proven to be correlated with suspended sediment concentration, turbidity etc., (Figure 7-1), the correlations explain relatively little of the scatter that is evident when particulate concentrations are low (which is the case on most occasions).



**Figure 7-1: Scatter plots illustrating the relationships between Secchi disk depth and candidate water-quality properties that have been measured.** Left hand images: data from Queen Charlotte Sound; right-hand images: data from Pelorus Sound. Note that the ranges spanned by corresponding x-axes and y-axes in the Queen Charlotte and Pelorus plots differ.

## 8 Acknowledgements

We are grateful to the crew and Marlborough District Council staff who collected the data.

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## Appendix A Methods for phytoplankton and zooplankton counts

Phytoplankton > approximately 3  $\mu\text{m}$ , microzooplankton and zooplankton were identified and enumerated in 200 ml subsamples preserved with Lugol's Iodine solution (1% final concentration) using a Leica DMI3000B inverted microscopic. For enumeration, samples were left to settle for >48 h before removing the supernatant and resettling in 10 ml Utermöhl chambers for at least 8 hrs. Samples are then counted and identified with an inverted microscope at 100 x to 600 x magnification. For phytoplankton the dimensions of each taxon were measured and the biovolume estimated from approximated geometric shapes (spheres, cones, ellipsoids), (Hillebrand, Dürselen et al. 1999; Olenina, Hajdu et al. 2006). Phytoplankton biovolumes were then used to calculate cell carbon ( $\text{mg C m}^{-3}$ ) using the regression equations of Menden-Deuer, Lessard (2000) for dinoflagellates and cyanobacteria, that of Cornet-Barthaux, Armand et al. (2007) for diatoms. In the same samples microzooplankton and zooplankton were identified to genus where possible and enumerated but with no differentiation of plastidic ciliates. Ciliate biomass was estimated from dimensions of 10-20 randomly chosen individuals of each taxon. The volumes were estimated from approximate geometric shapes and were converted to carbon biomass using a factor of  $0.19 \text{ pg C } \mu\text{m}^{-3}$  (Putt and Stoecker 1989). The use of Lugol's iodine for preservation may have resulted in an underestimation of biomass as a result of cell shrinkage.

For both phytoplankton and microzooplankton the whole chamber was scanned for the enumeration of larger cells. For these the detection limit is 1 in 200 ml's for smaller cells. detection limits vary depending on the magnification and the number of Fields of View (FOV) counted. Our counts are conducted with a minimal of 20 FOV.

### Counting Random Field

When the distribution of algal objects in the settling chamber can be considered random and conforming to a Poisson distribution, the number of fields or algal objects to count can be set according to what level of precision or detection is required, as the precision/detection limit is dependent on the number of algal objects/fields. The precision (confidence limits) for our methods are given below.

**Table A-1: Cell count accuracy.** (Lund, Kipling et al. 1958)

Cell no. counted	Accuracy expressed as % of count (95% confidence limits)	Comment
4	+/- 100	
16	+/- 50	
100	+/- 20	=100 units / unicells
400	+/- 10	
1600	+/- 5	

The detection limit calculations are given below. These are calculated for each lens and settling chamber combination presented. The precision (D) of a count can be expressed as either (i) the standard error as a proportion of the mean, or (ii) 95% confidence limits as a proportion of the mean.

NOTE: the precision relates to the type of algal objects counted. If only a single species is to be counted, then the precision should be set for that species; if all taxa are to be counted, then the precision is set for the total number of algal objects. For accredited cell counts, the precision is pre-set.

## Detection Limit

The detection limit is an important parameter in phytoplankton surveys. It is defined as the minimum concentration of a specific taxon that will be detected with 99% certainty. Below this limit, detection is a matter of chance. This also implies, that if a particular species has been found, its concentration does not necessarily need to be above the detection limit. The limit of detection does not take account of the skill of the analyst (e.g., algae that are overlooked). The limit of detection, from an identification point of view, corresponds with the laboratory species list.

By contrast to estimates of precision, the detection limit is dependent on the number of fields counted (actually the absolute volume of viewed sample) rather than the number of algal objects. If the number of algal objects to be counted is fixed, then a variation in the detection limit may occur within the same sample series. The detection limit also applies to the size of algal objects. At a magnification of 400–600x, the smallest countable particles have a size of circa 2 to 4  $\mu\text{m}$ .

**Table A-2: Microscope calibration.** Description - New Leica. Calculated detection limits in *cells per ml* for 20 FOV (fields of view) for each lens for Settling Chambers of the given diameter.

Objective lens	Settling chamber diameter (mm)		
	26	25	24
x63	693.5	641.2	590.9
x40	271.9	251.4	231.7
x20	67.4	62.3	57.4
x10	16.7	15.4	14.2
x5	4.2	3.9	3.6

The probability with which an object is detected can be determined by Poisson statistics according to:

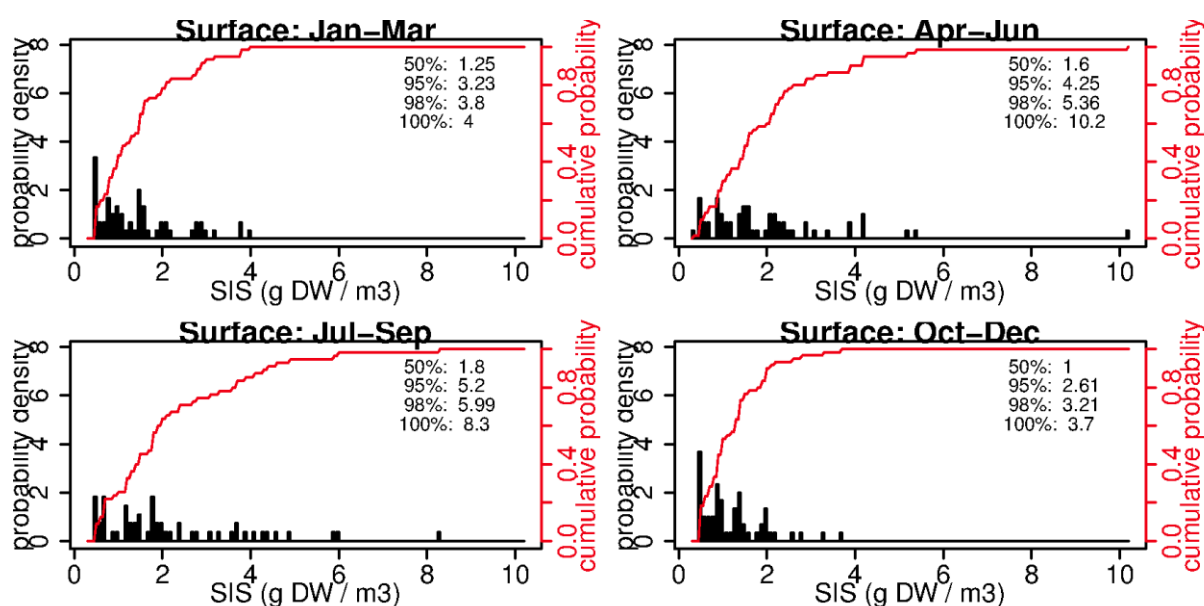
$$n_{\text{det}} = -\ln(\alpha) \cdot f_{\text{total}} / (V \cdot f_{\text{counted}})$$

where  $\alpha$  is the level of significance,  $n_{\text{det}}$  is the detection limit,  $f_{\text{total}}$  is the total number of microscope fields in the settling chamber,  $f_{\text{counted}}$  is the number of fields counted,  $V$  is the volume of the sub-sample in the settling chamber.

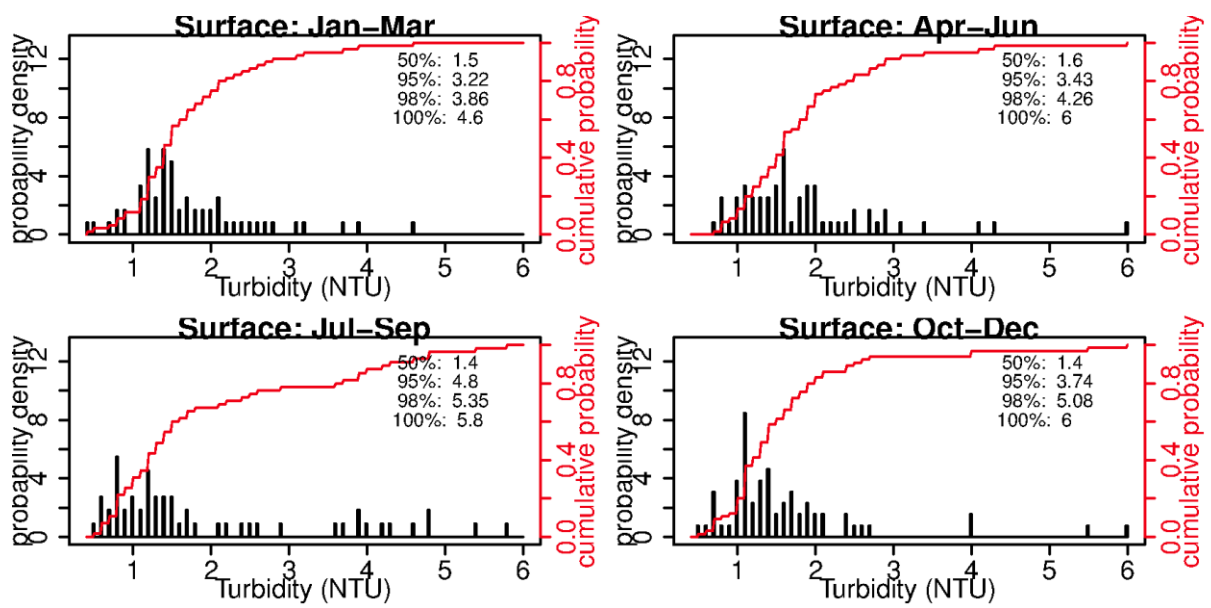
In multi-taxon samples  $\alpha$  must be corrected for the number of taxa. The chance of finding each taxon in a sample is determined by the product of the probabilities of each independent taxon. This implies literally that if, for instance, ten taxa each have a concentration equal to the detection limit,  $n_{\text{det}}$ , the probability that they will all be detected in the same counting at  $\alpha = 0.01$  is only  $100 \times (1-0.01) \times 10 = 90\%$ . Any knowledge of taxon richness of a sample prior to analysis can be used to correct  $\alpha$  and determine a proper detection limit or the number of fields one has to count. In some studies an  $\alpha$  of 0.01 will be sufficient whereas in other studies an  $\alpha$  of 0.001 or even less is necessary.

## Appendix B Probability distributions in the Queen Charlotte water-quality data

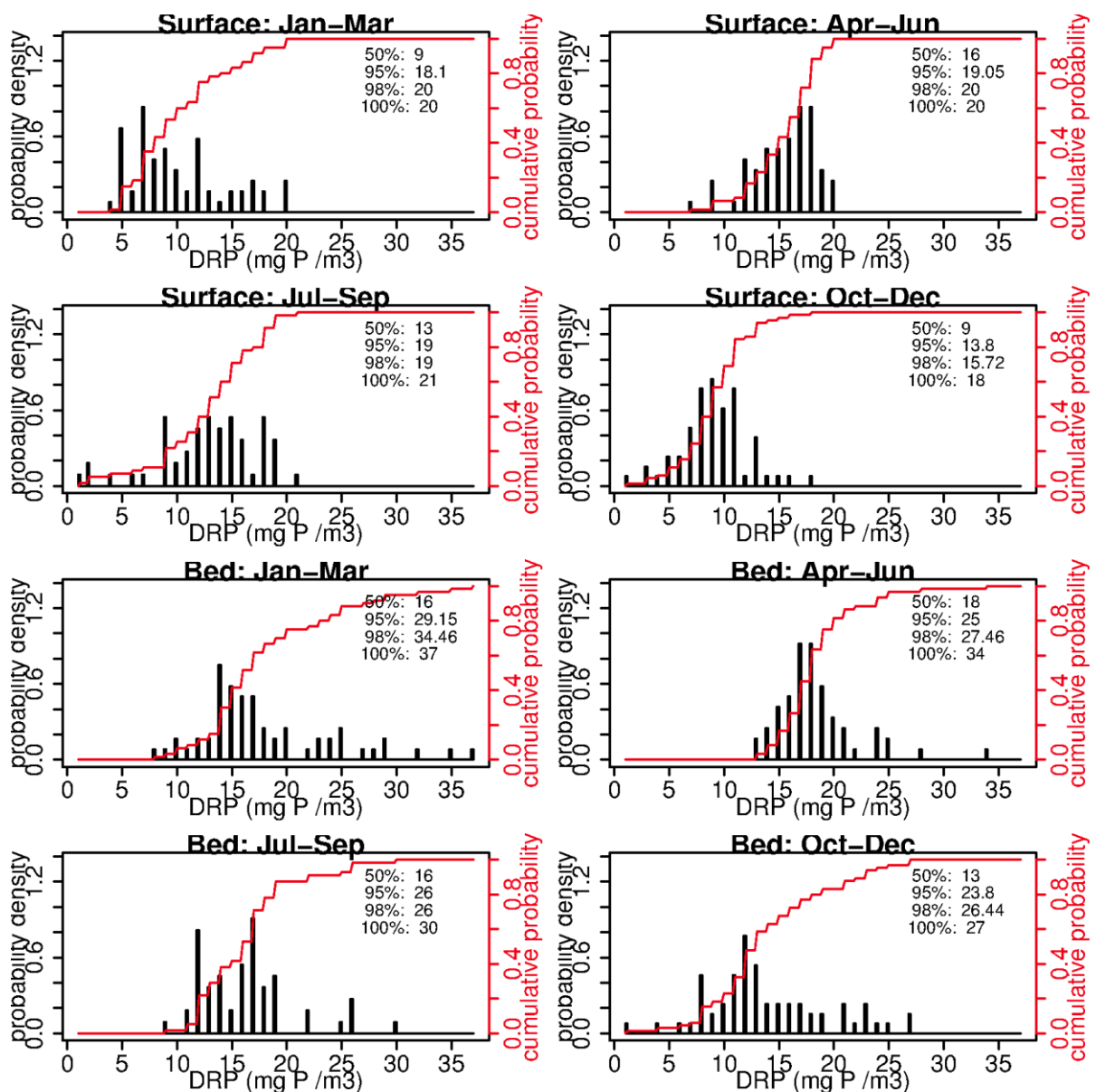
The following figures illustrate the probability distributions of the recorded water-quality values. For each quantity, records were aggregated by position-within-water-column (near-surface or near-bed) and season-of-year. The members of each aggregate were then binned into bands of concentration/abundance and the number of records within each bin was recorded. Note that no distinction is drawn between the different stations (PLS-1 – PLS-7). Data-records which Table 6-1 describes as having been rejected were also rejected prior to this analysis.



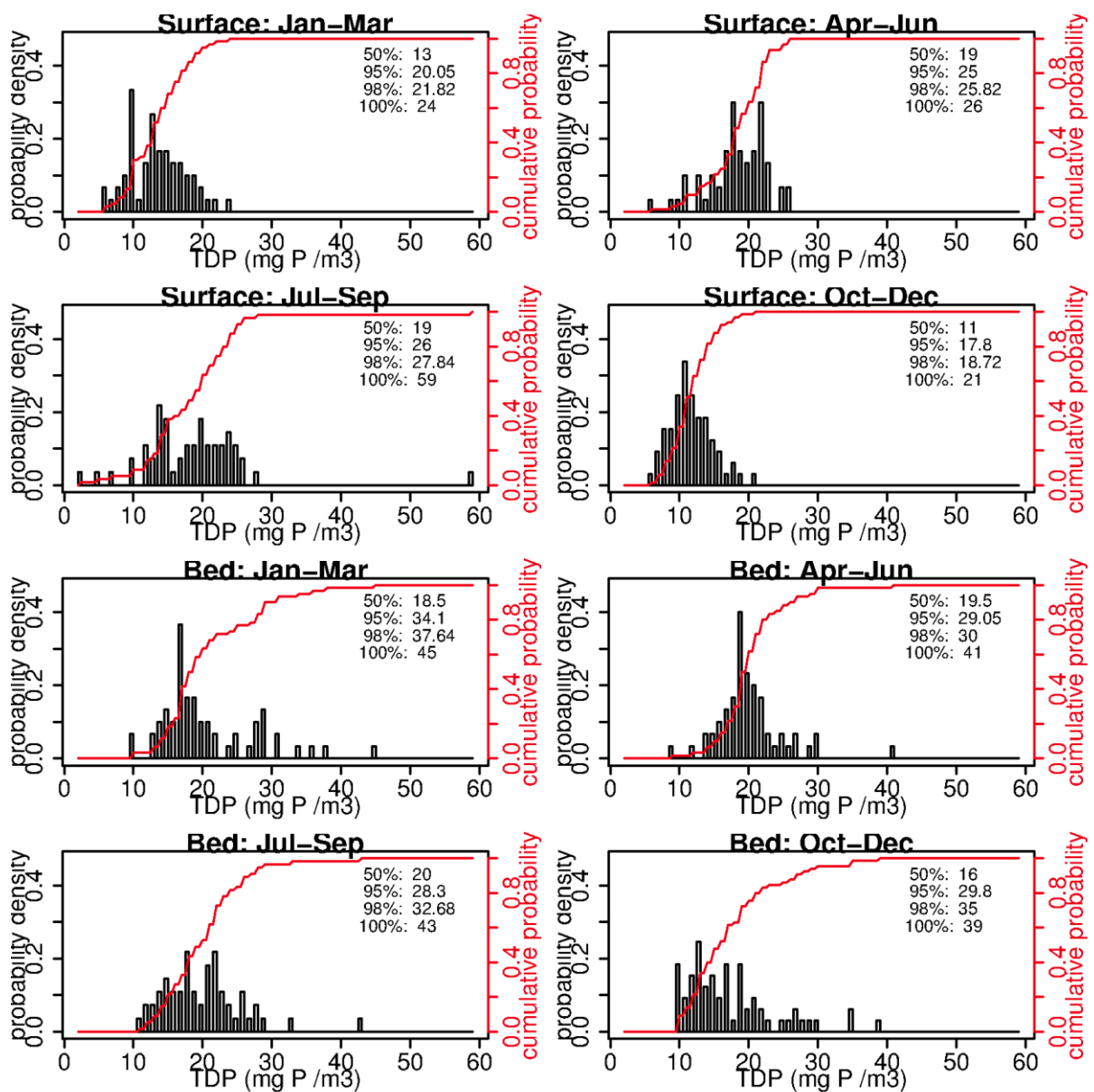
**Figure B-1:** Empirical probability density distributions for the concentration of near-surface suspended inorganic solids in Queen Charlotte Sound/Tory Channel. The inset text indicates the concentrations corresponding to the 50 (i.e., median), 95, 98 and 100 percentiles.



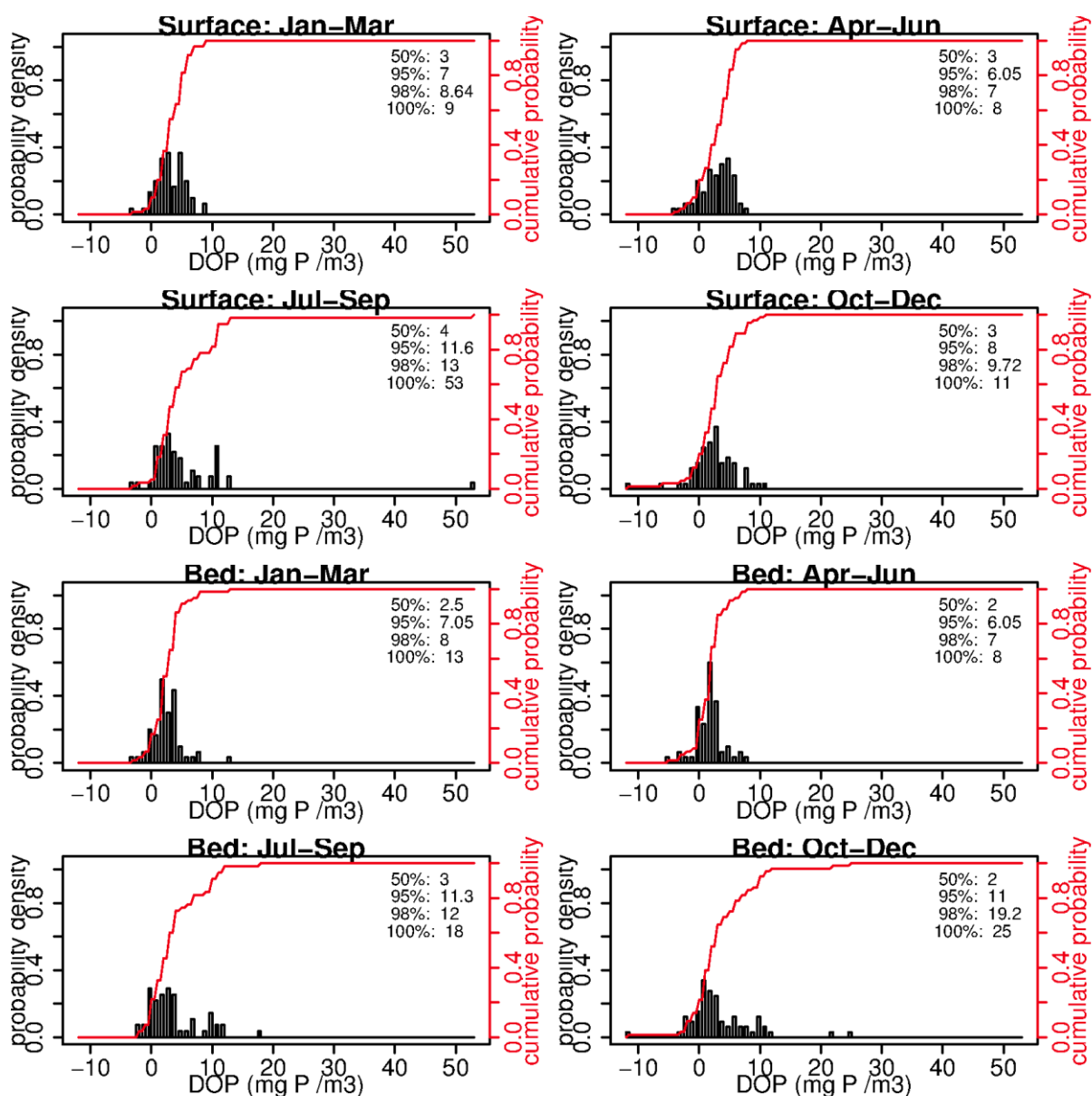
**Figure B-2: Empirical probability density distributions for near-surface turbidity in Queen Charlotte Sound/Tory Channel.**



**Figure B-3: Empirical probability density distributions for near-surface and near-bed dissolved reactive phosphorus in Queen Charlotte Sound/Tory Channel.**

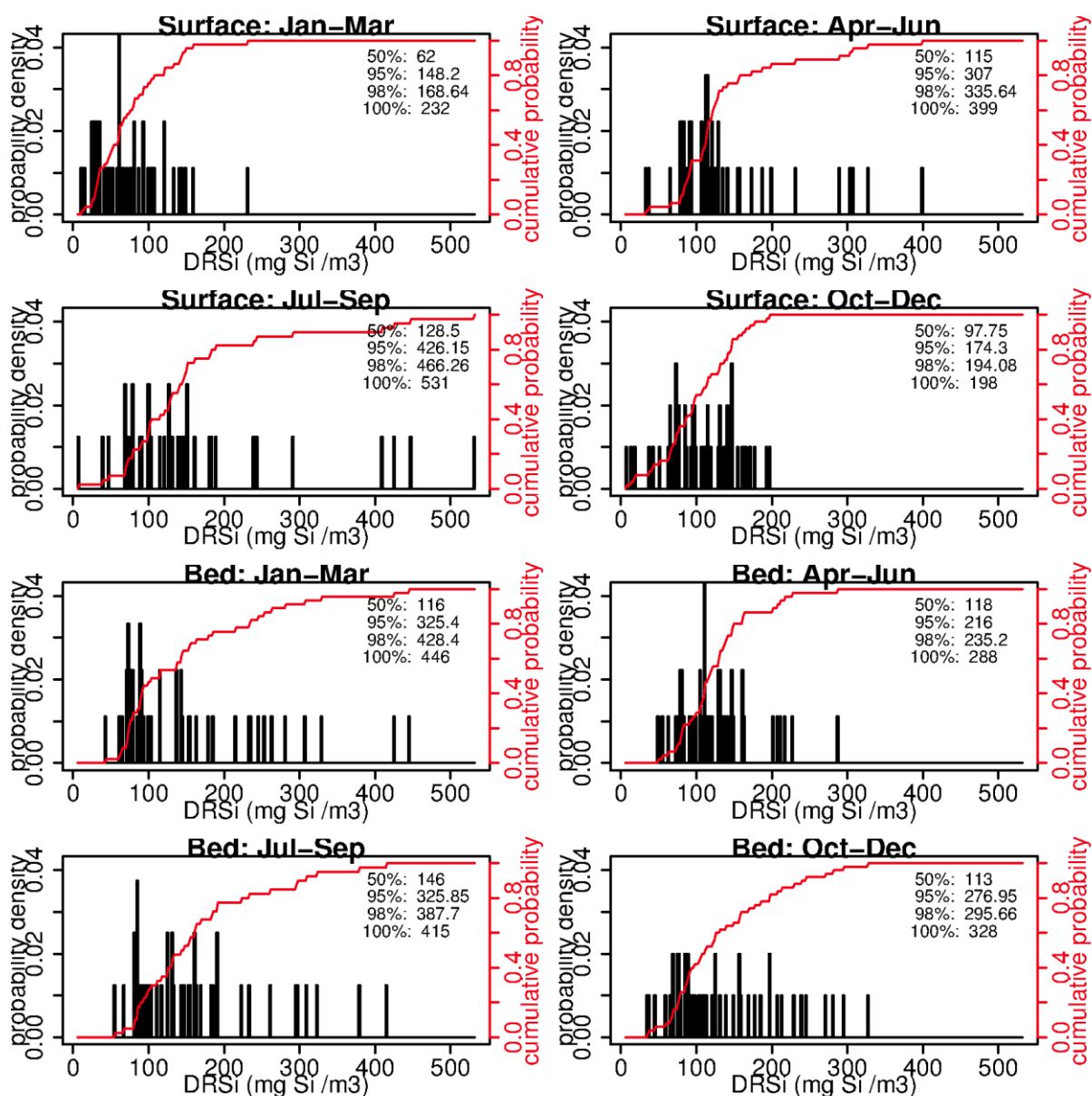


**Figure B-4: Empirical probability density distributions for near-surface and near-bed total dissolved phosphorus in Queen Charlotte Sound/Tory Channel.**

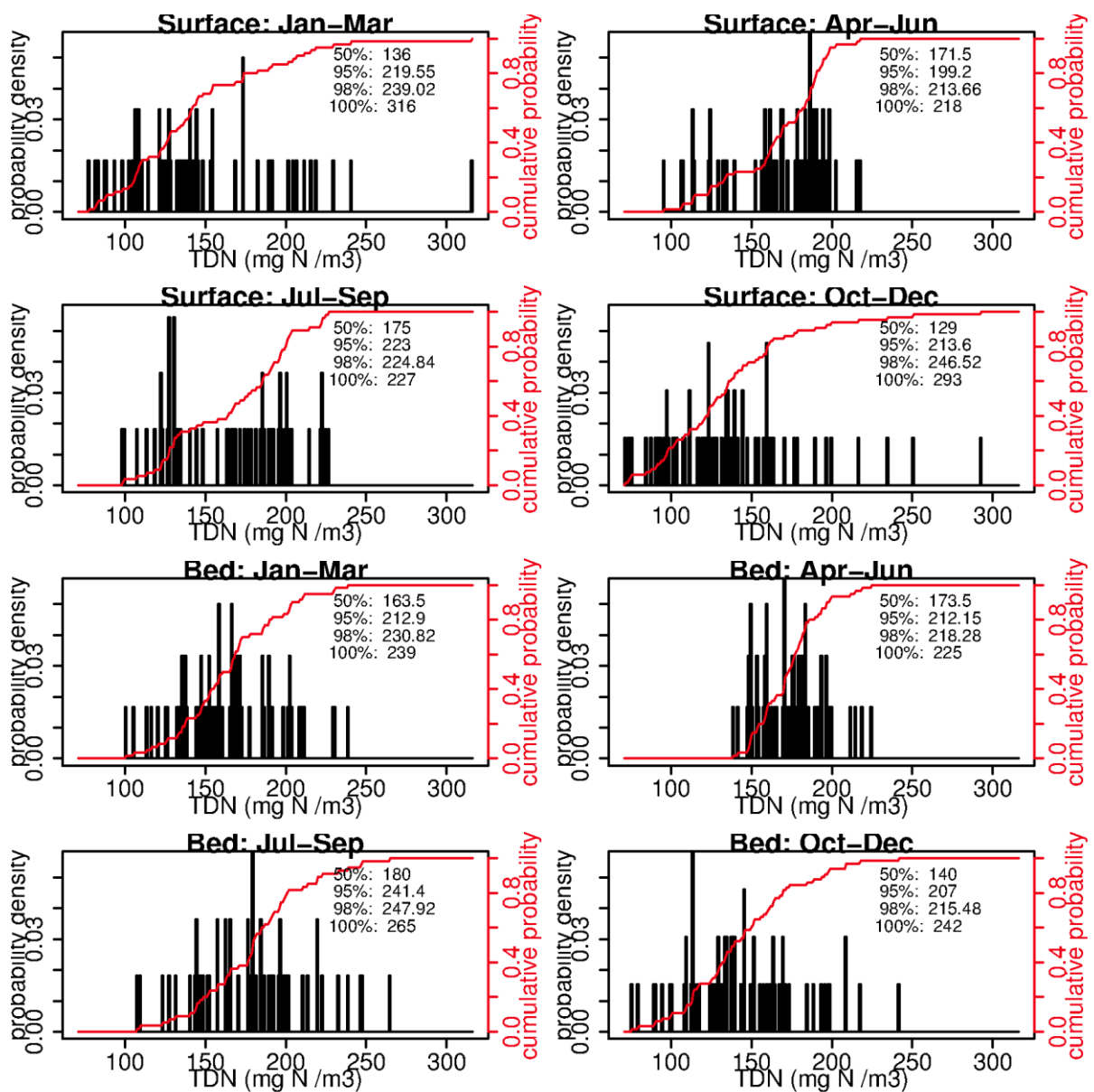


**Figure B-5: Empirical probability density distributions for near-surface and near-bed dissolved organic phosphorus in Queen Charlotte Sound/Tory Channel.** Dissolved organic phosphorus is calculated by difference; measurement errors in the underlying terms for TDP and DRP can (seemingly) induce negative DOP.

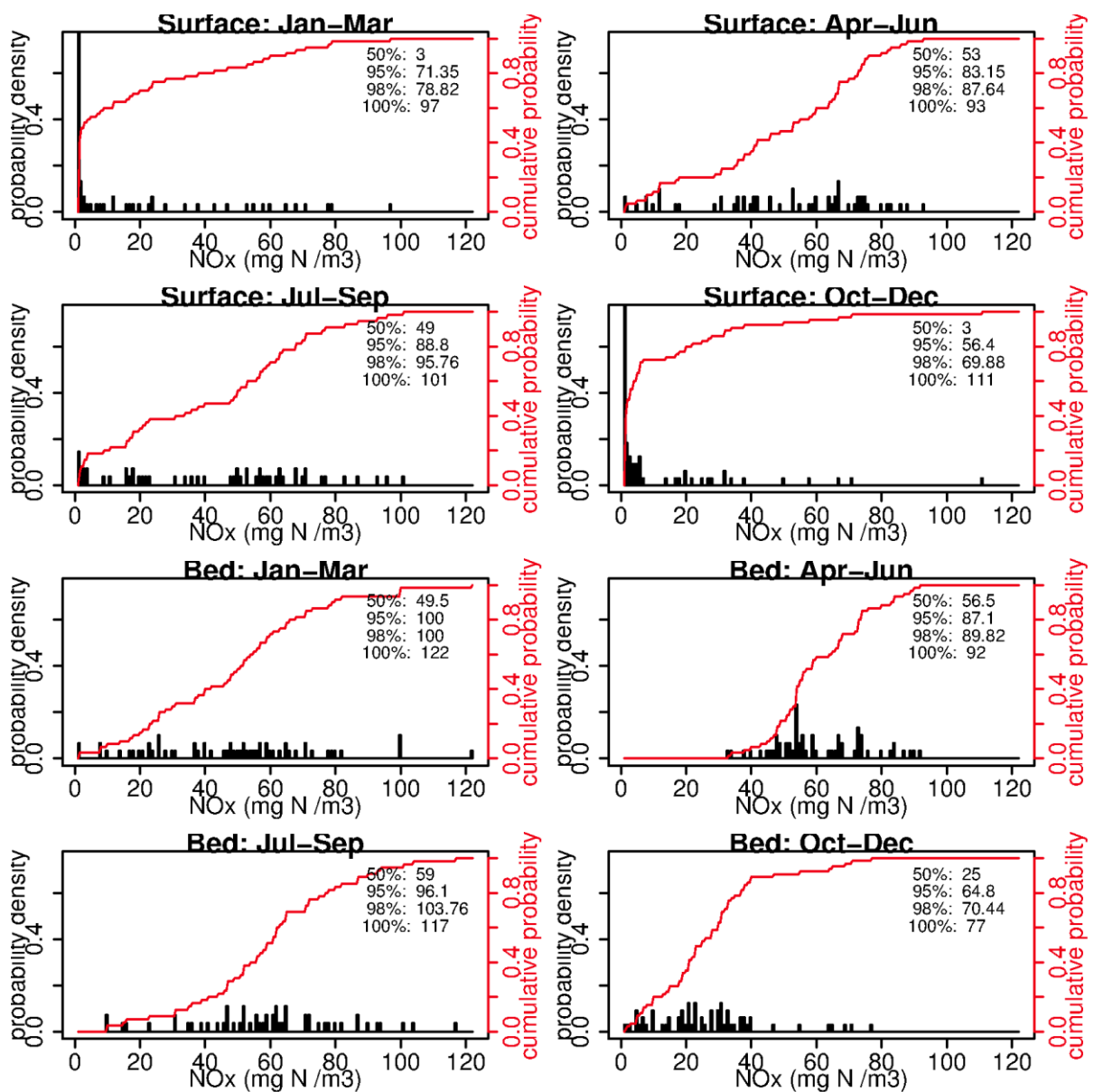




**Figure B-6: Empirical probability density distributions for near-surface and near-bed dissolved reactive silicon in Queen Charlotte Sound/Tory Channel.**



**Figure B-7: Empirical probability density distributions for near-surface and near-bed total dissolved nitrogen in Queen Charlotte Sound/Tory Channel.**



**Figure B-8: Empirical probability density distributions for near-surface and near-bed nitrate in Queen Charlotte Sound/Tory Channel.**

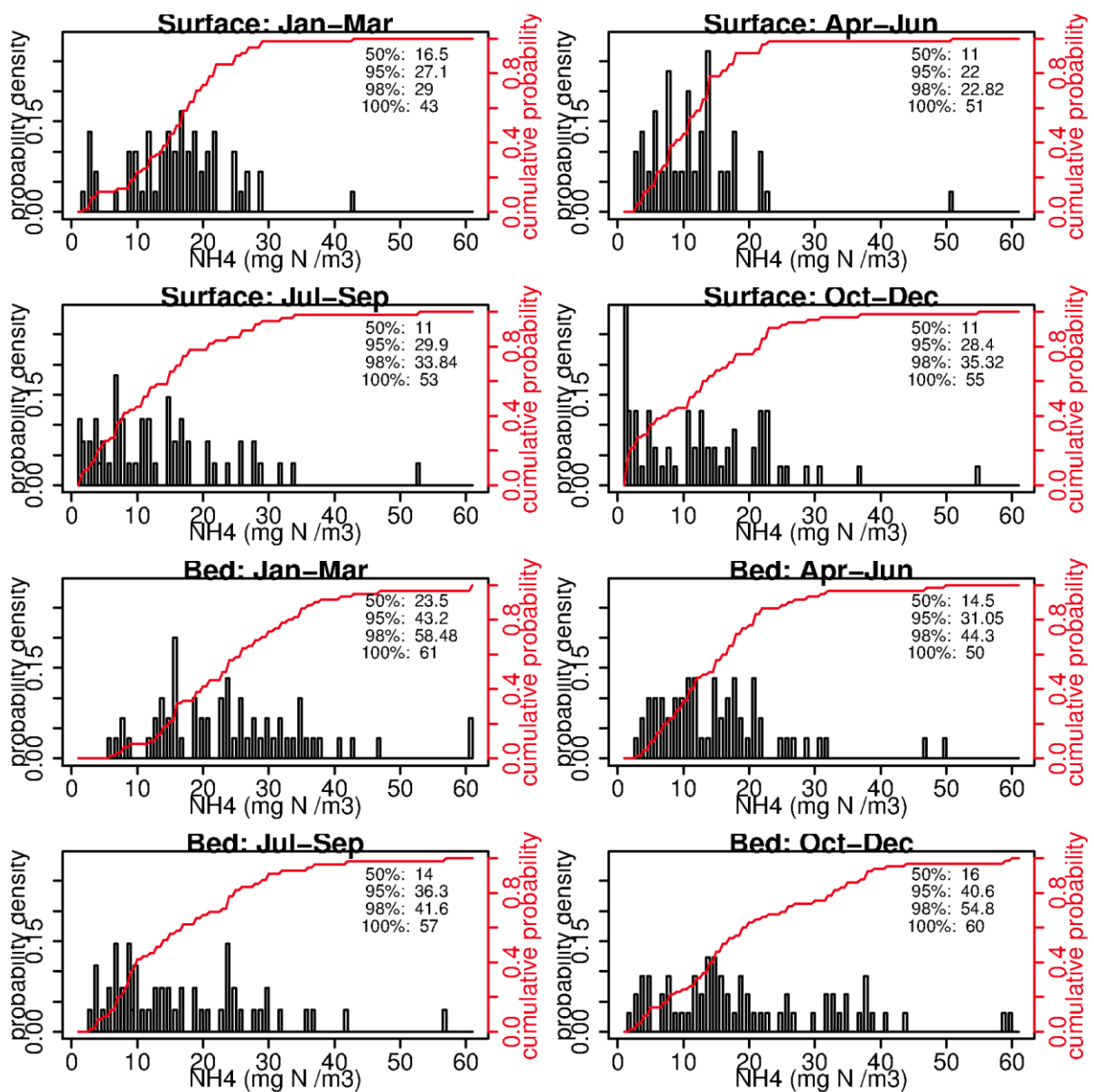


Figure B-9: Empirical probability density distributions for near-surface and near-bed ammoniacal nitrogen in Queen Charlotte Sound/Tory Channel.

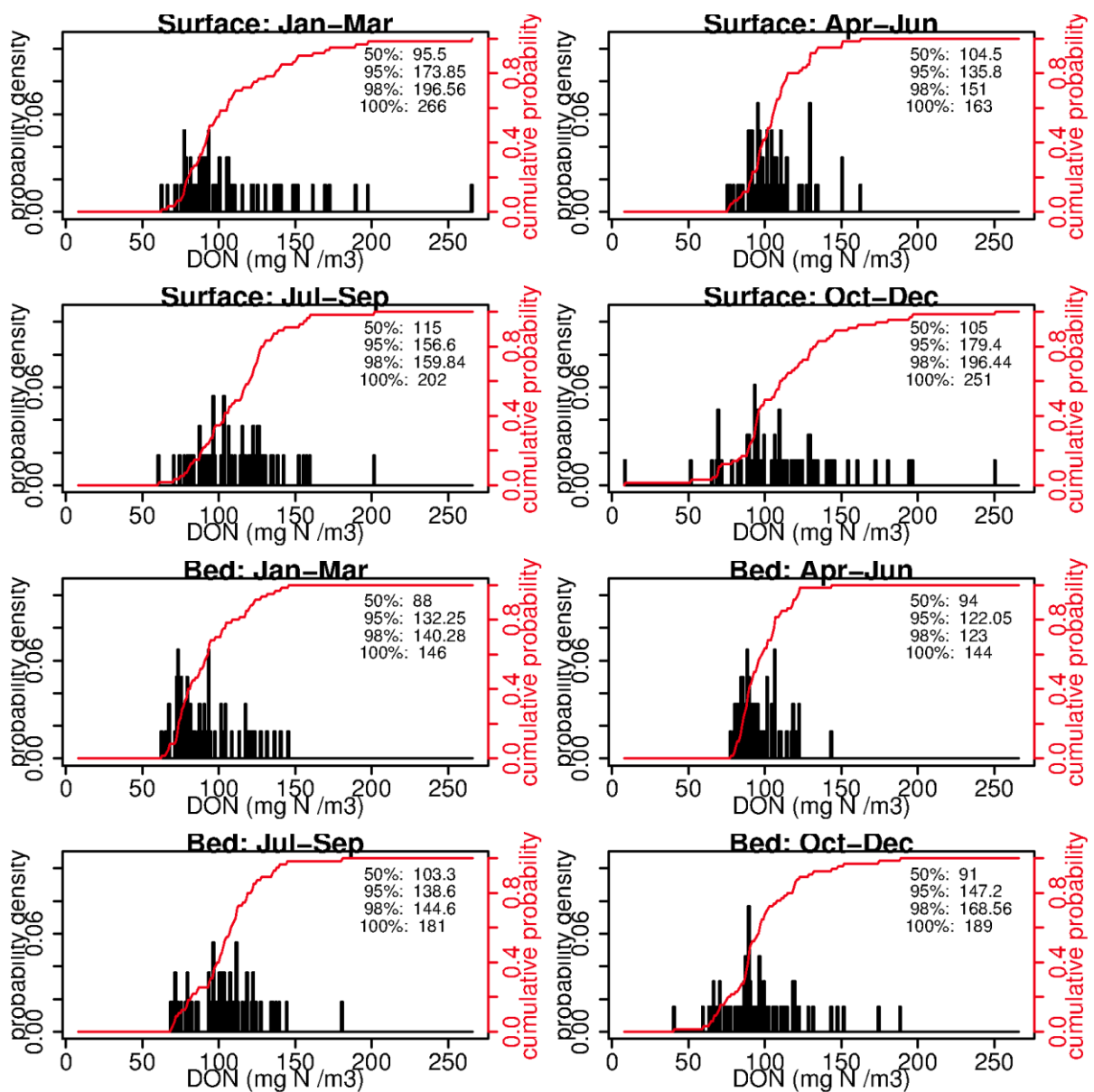
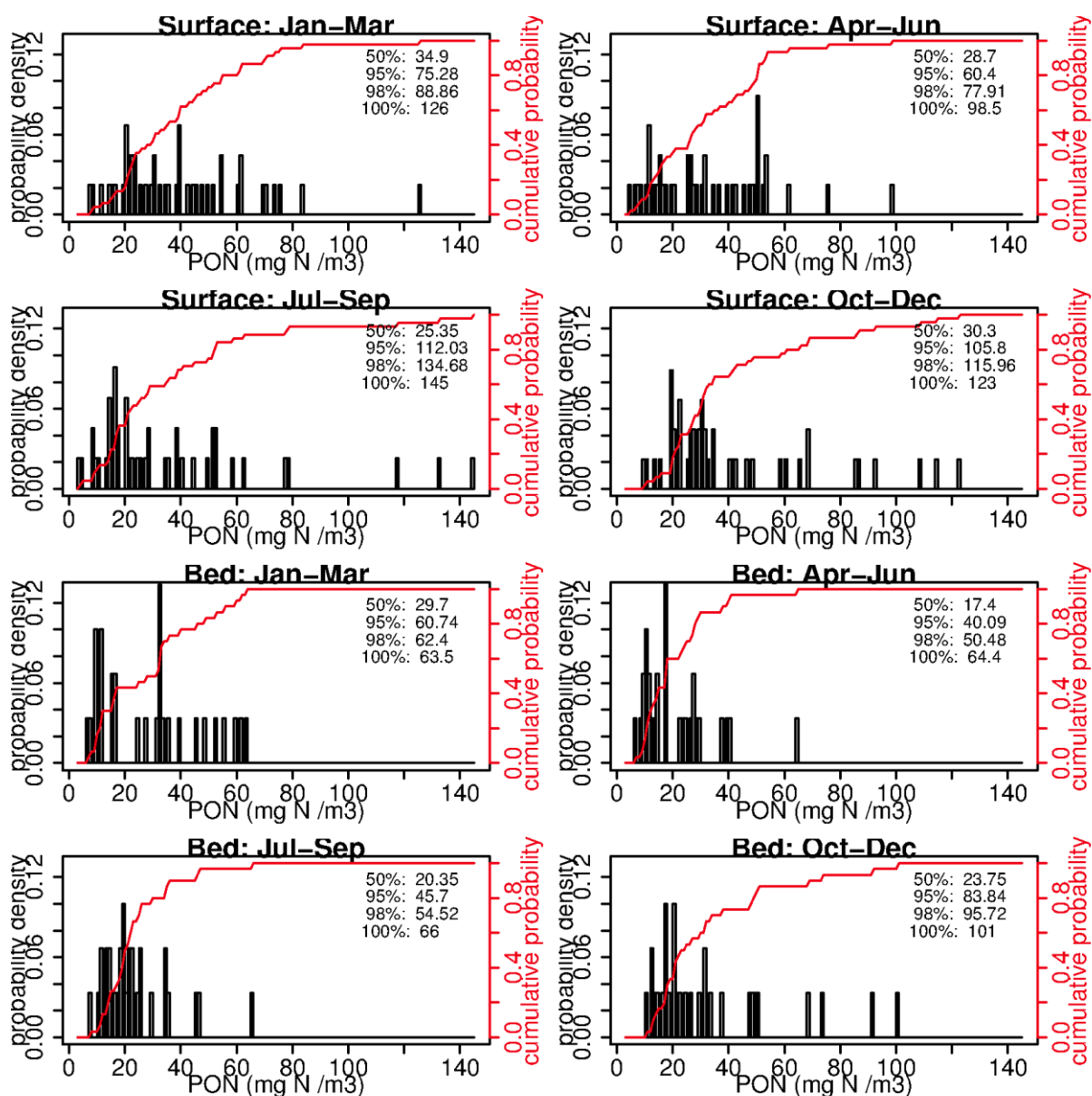


Figure B-10: Empirical probability density distributions for near-surface and near-bed dissolved organic nitrogen in Queen Charlotte Sound/Tory Channel.



**Figure B-11: Empirical probability density distributions for near-surface and near-bed particulate nitrogen (or particulate organic nitrogen in cases where that was measured instead) in Queen Charlotte Sound/Tory Channel.**

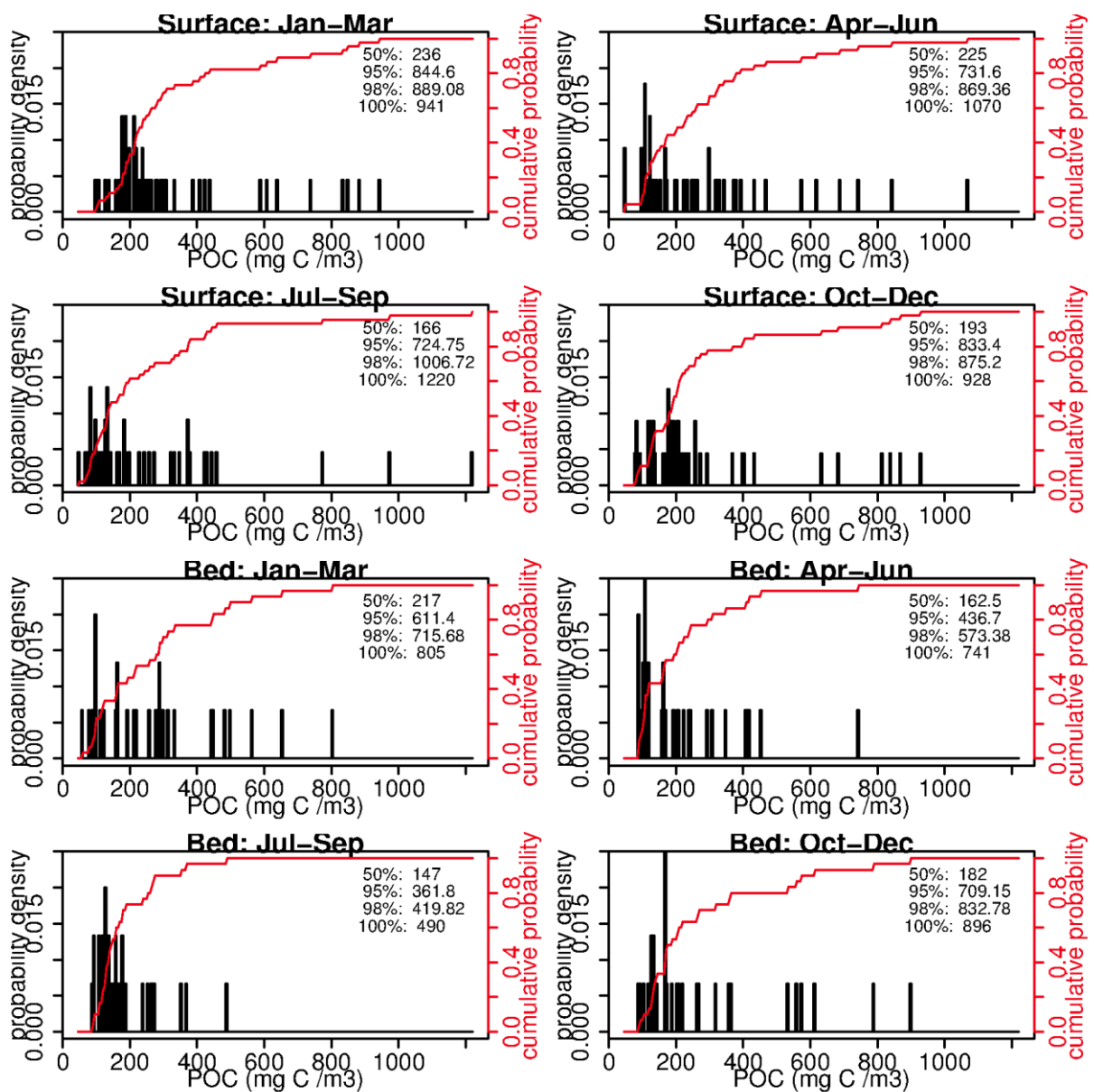


Figure B-12: Empirical probability density distributions for near-surface and near-bed particulate carbon (or particulate organic carbon where that was measured instead) in Queen Charlotte Sound/Tory Channel.

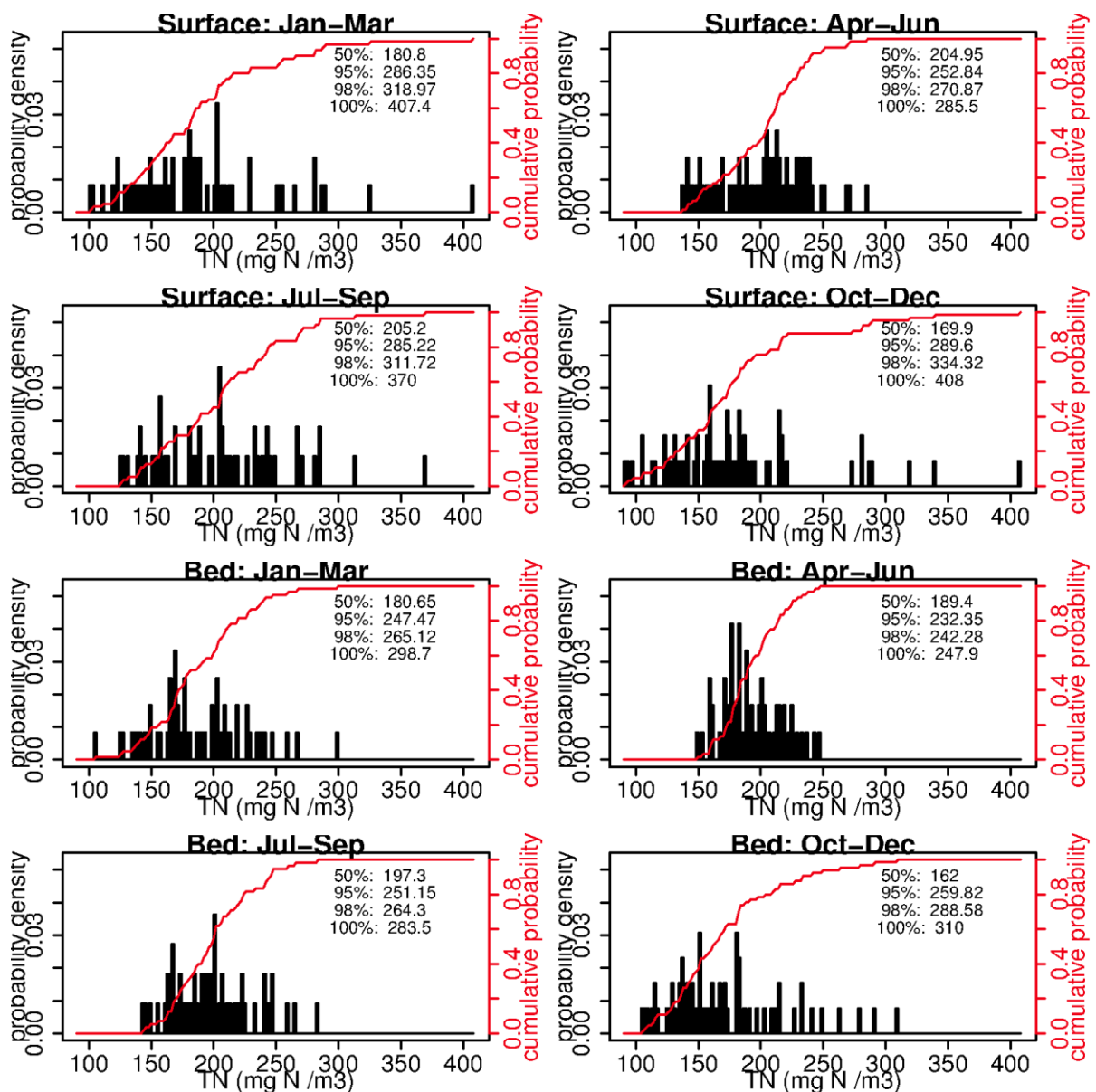
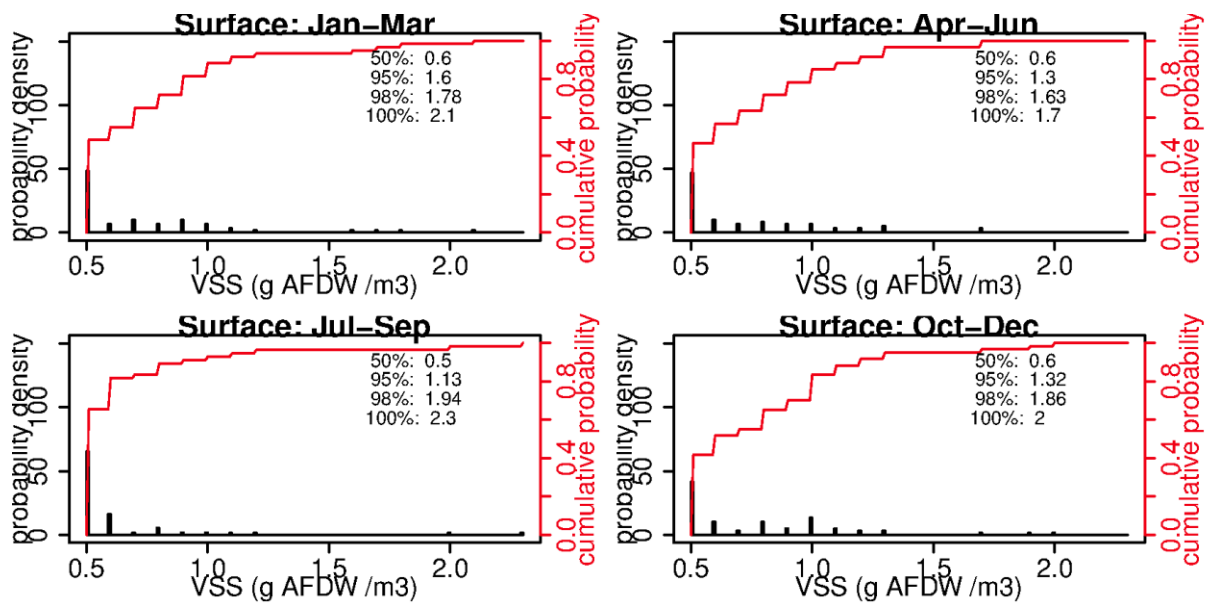


Figure B-13: Empirical probability density distributions for near-surface and near-bed total nitrogen in Queen Charlotte Sound/Tory Channel.





**Figure B-14: Empirical probability density distributions for near-surface volatile suspended solids in Queen Charlotte Sound/Tory Channel.**

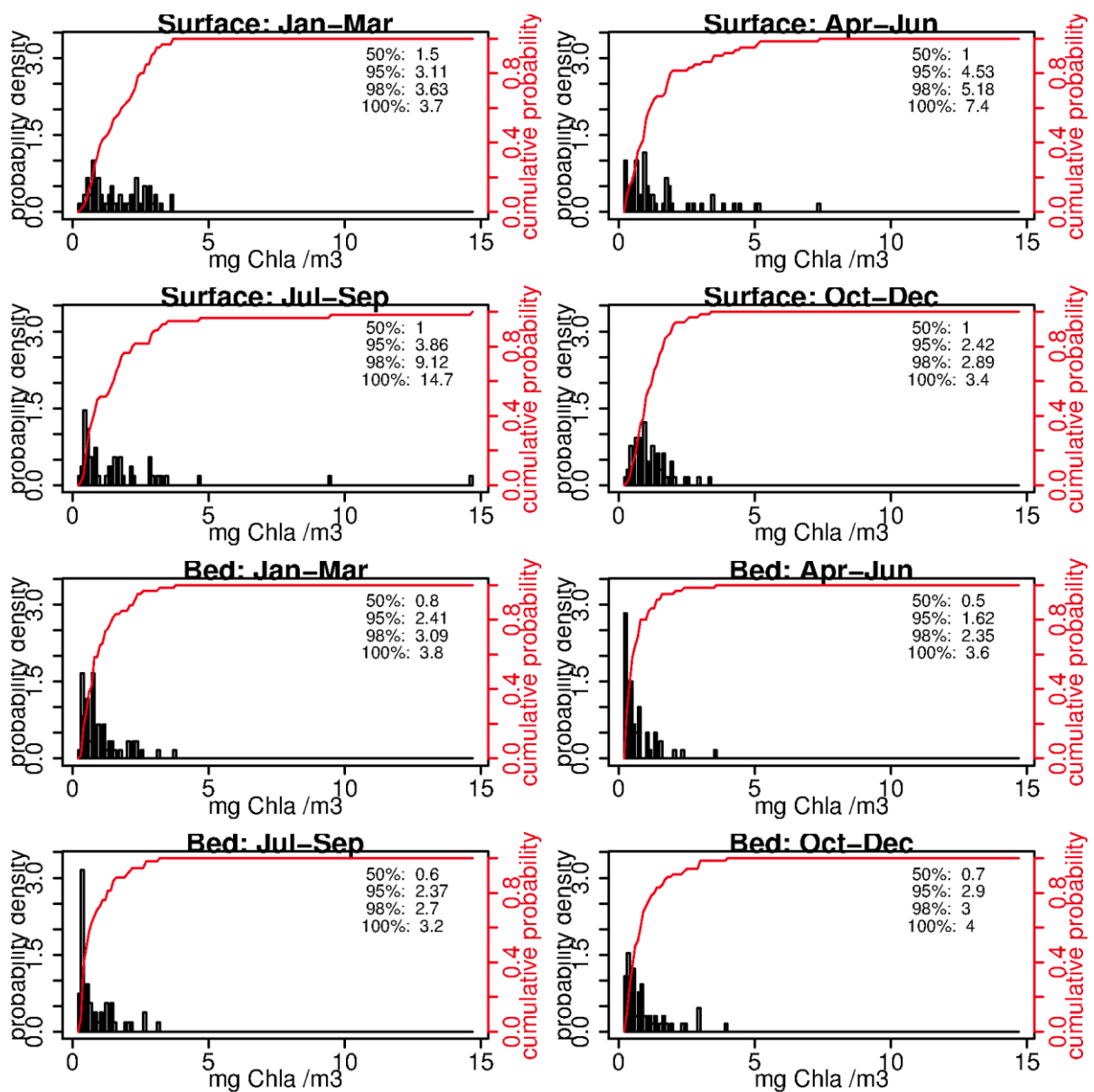
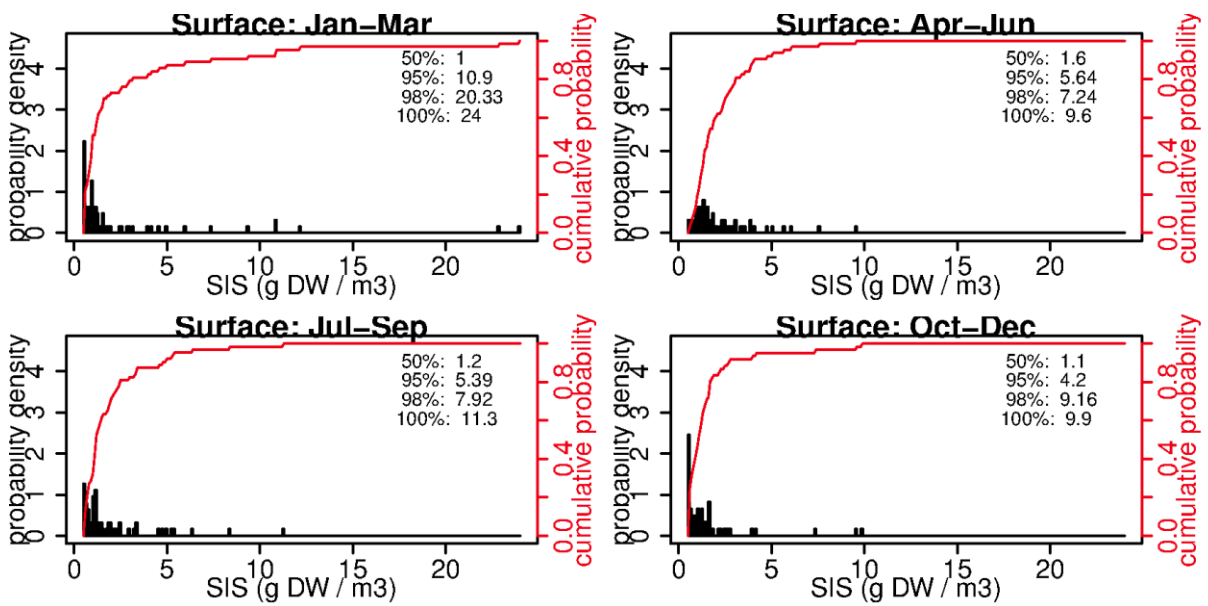


Figure B-15: Empirical probability density distributions for near-surface and near-bed chlorophyll concentration in Queen Charlotte Sound/Tory Channel.

## Appendix C Probability distributions in the Pelorus water-quality data

The following figures illustrate the probability distributions of the recorded water-quality values. For each quantity, records were aggregated by position-within-water-column (near-surface or near-bed) and season-of-year. The members of each aggregate were then binned into bands of concentration/abundance and the number of records within each bin was recorded. Note that no distinction is drawn between the different stations (PLS-1 – PLS-7). Data-records which Table 6-1 describes as having been rejected were also rejected prior to this analysis.



**Figure C-1:** Empirical probability density distributions for the concentration of near-surface suspended inorganic solids in Pelorus Sound.

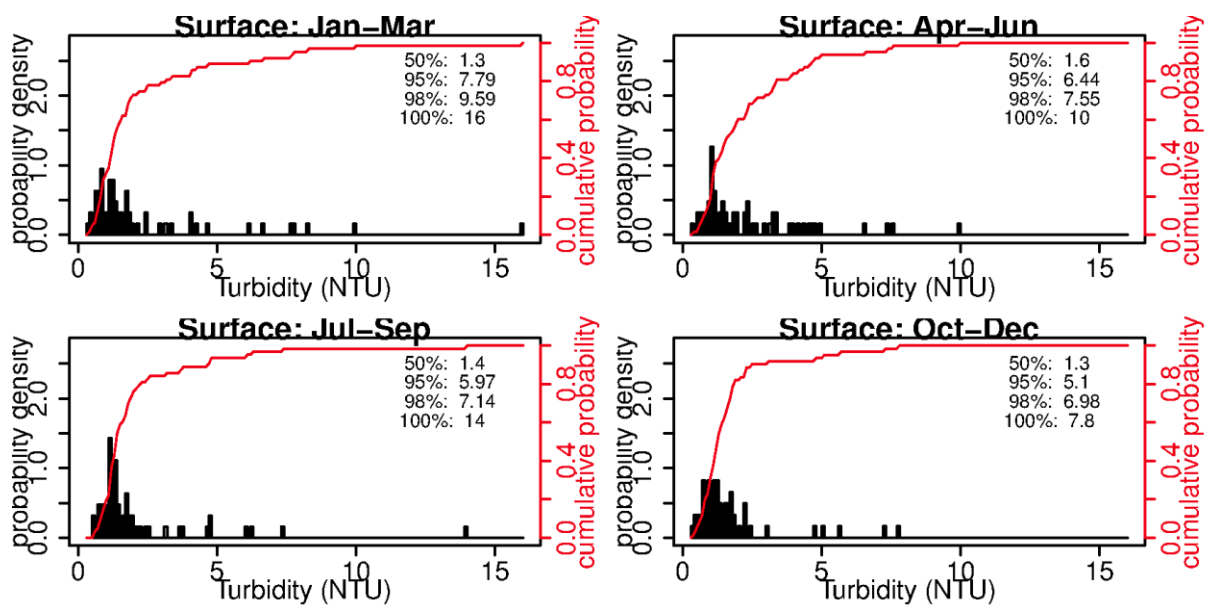
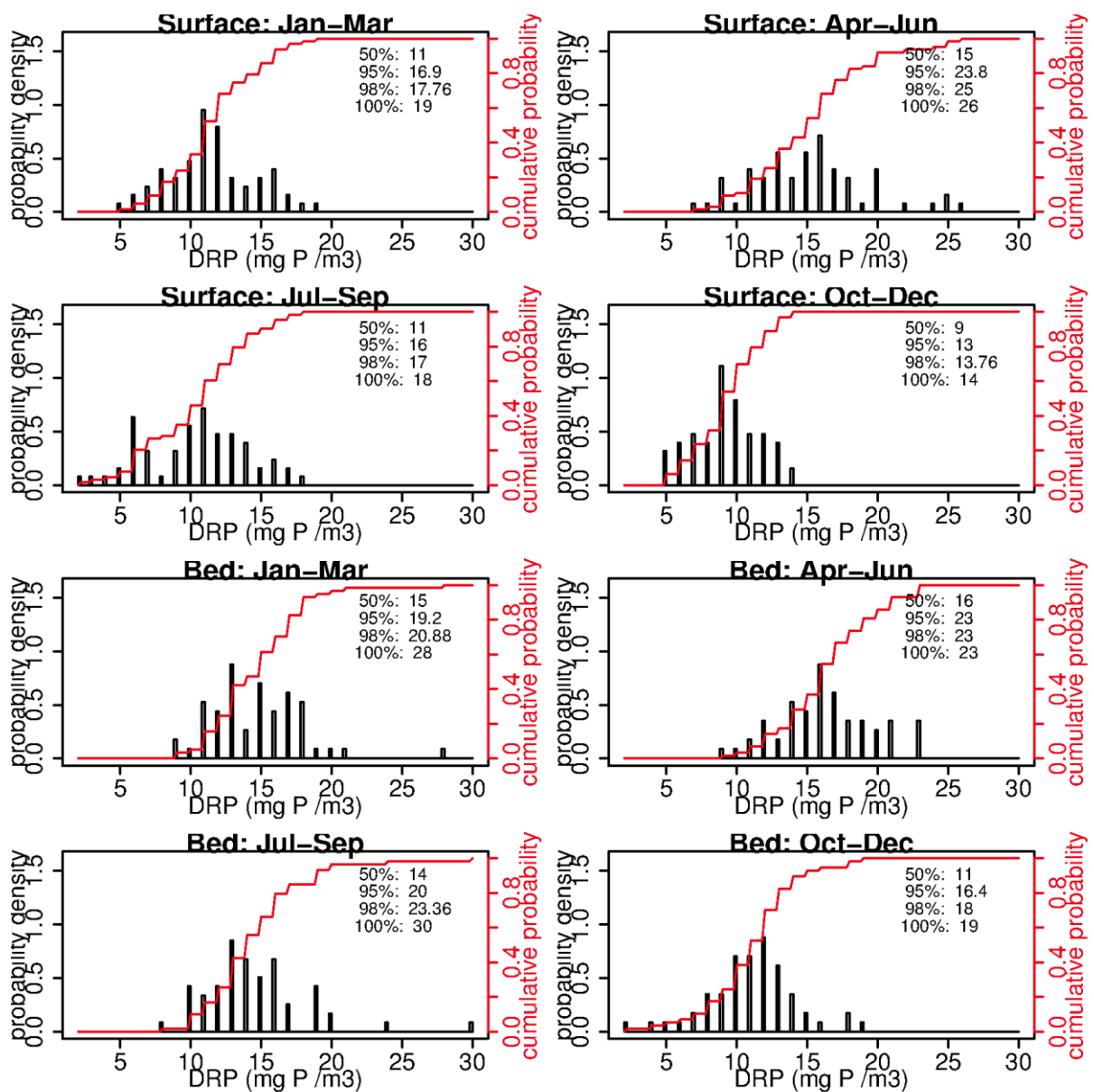


Figure C-2: Empirical probability density distributions for near-surface turbidity in Pelorus Sound.



**Figure C-3: Empirical probability density distributions for near-surface and near-bed dissolved reactive phosphorus in Pelorus Sound.**

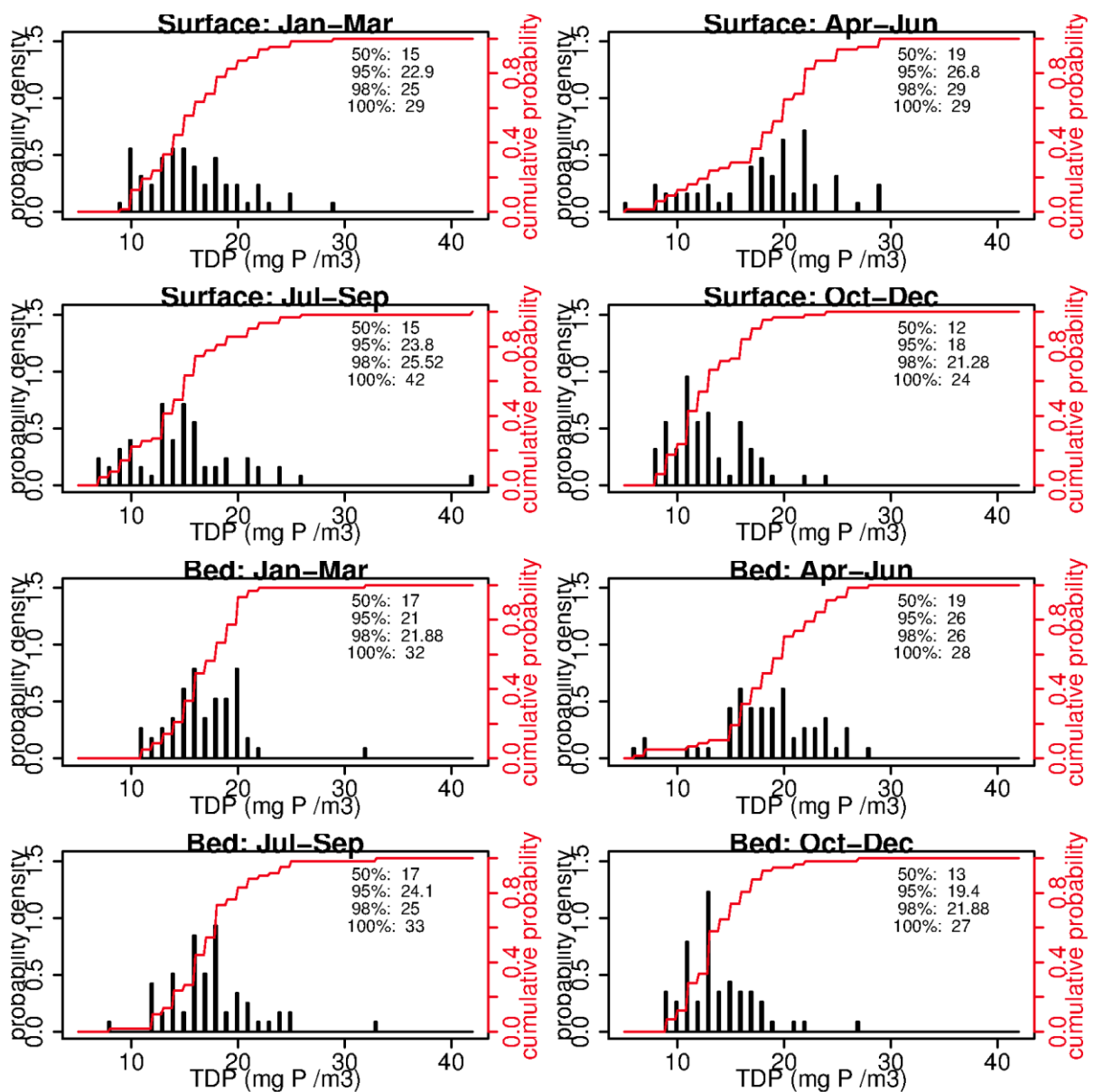
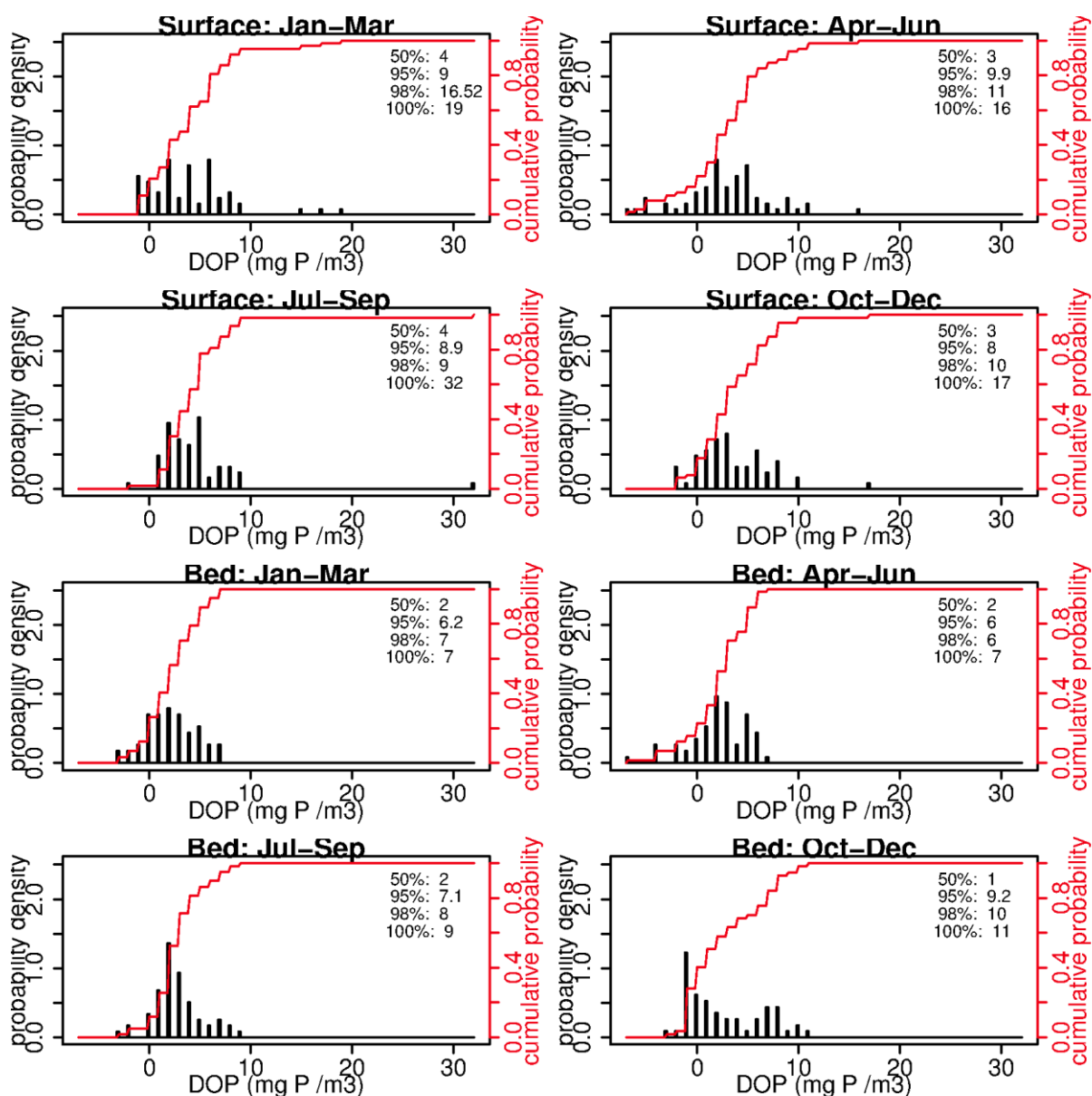


Figure C-4: Empirical probability density distributions for near-surface and near-bed total dissolved phosphorus in Pelorus Sound.



**Figure C-5: Empirical probability density distributions for near-surface and near-bed dissolved organic phosphorus in Pelorus Sound.** Dissolved organic phosphorus is calculated by difference; measurement errors in the underlying terms for TDP and DRP can (seemingly) induce negative DOP.

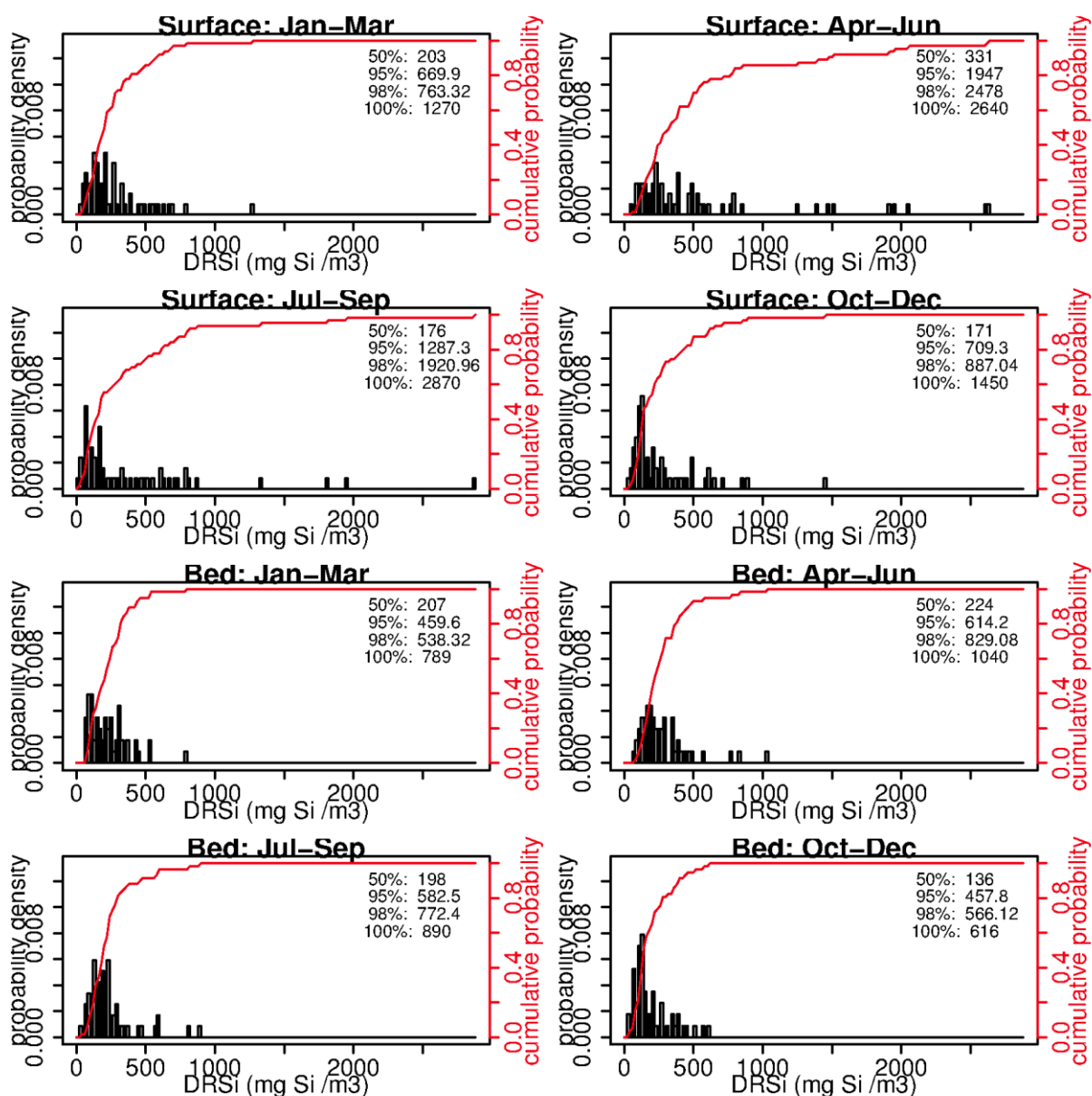
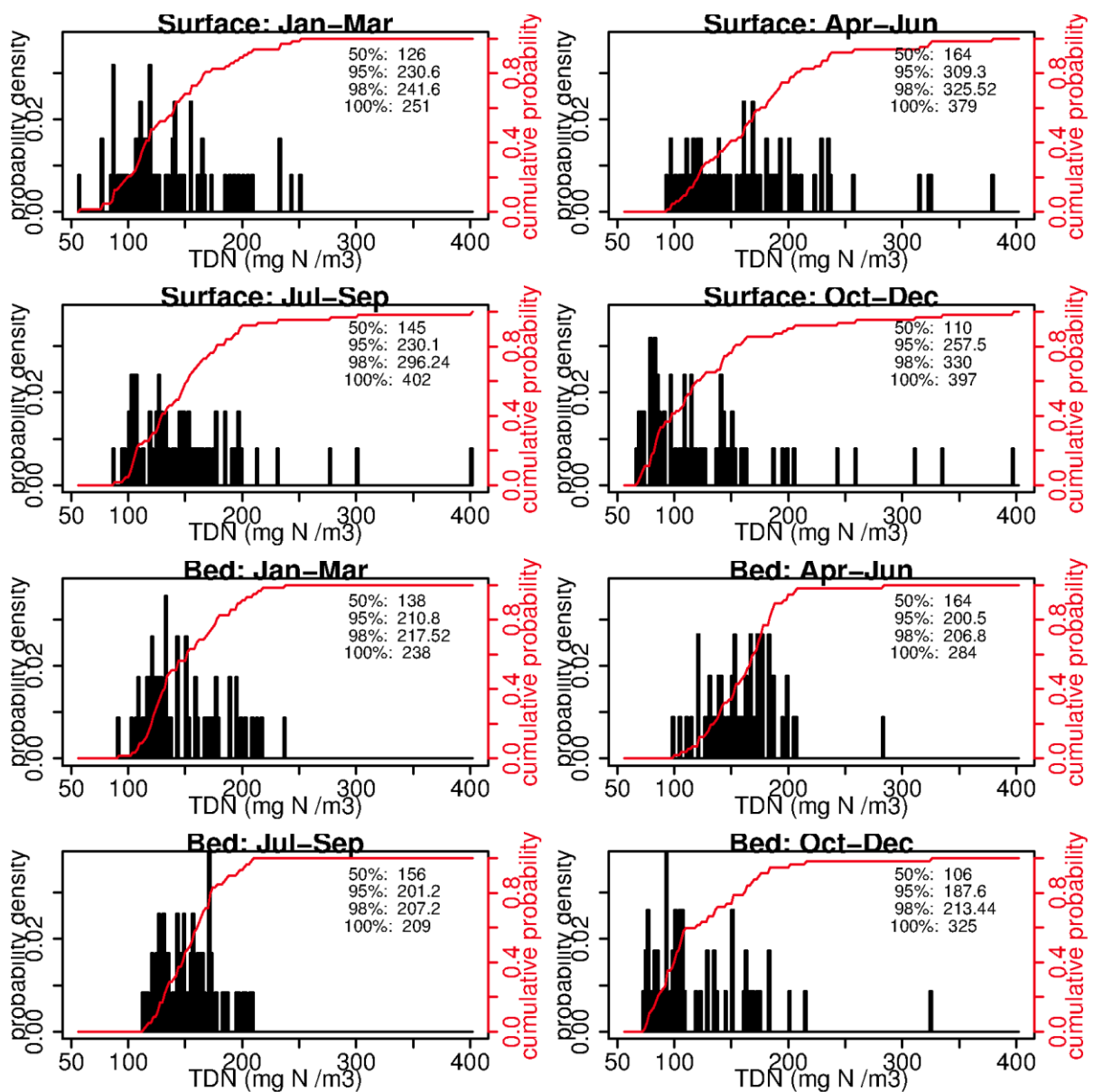


Figure C-6: Empirical probability density distributions for near-surface and near-bed dissolved reactive silicon in Pelorus Sound.





**Figure C-7: Empirical probability density distributions for near-surface and near-bed total dissolved nitrogen in Pelorus Sound.**

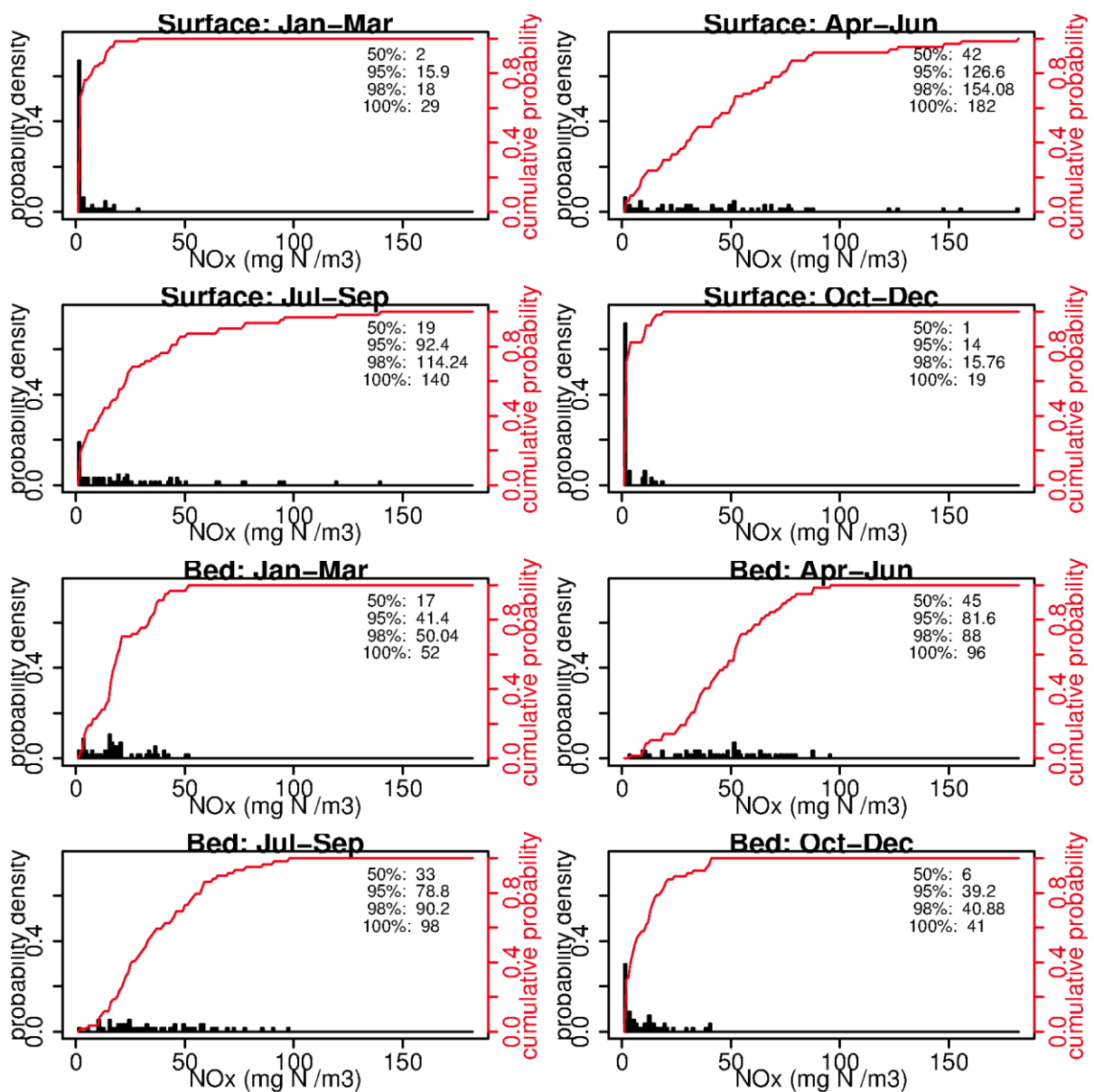


Figure C-8: Empirical probability density distributions for near-surface and near-bed nitrate in Pelorus Sound.

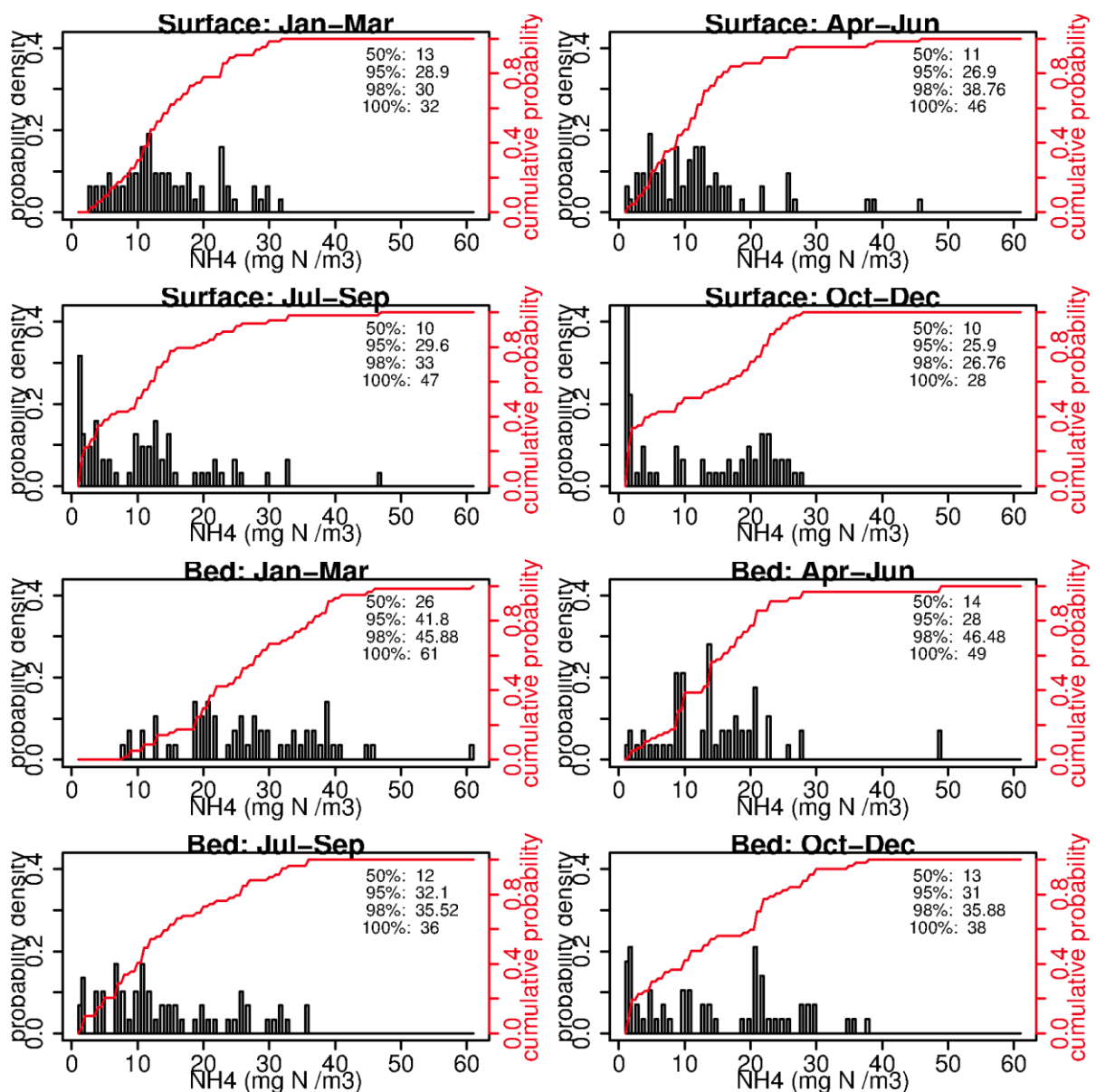


Figure C-9: Empirical probability density distributions for near-surface and near-bed ammonical nitrogen in Pelorus Sound.

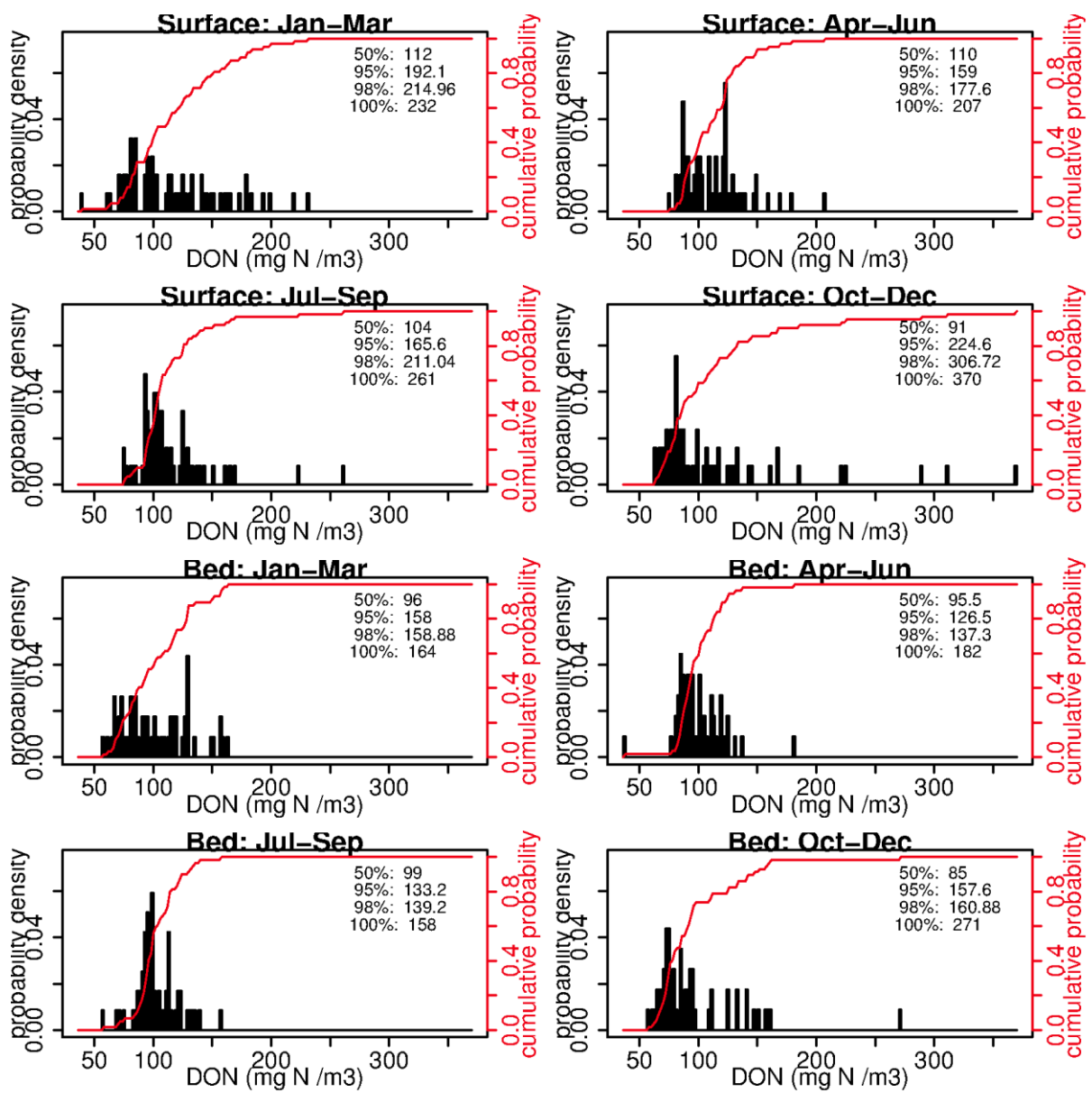


Figure C-10: Empirical probability density distributions for near-surface and near-bed dissolved organic nitrogen in Pelorus Sound.

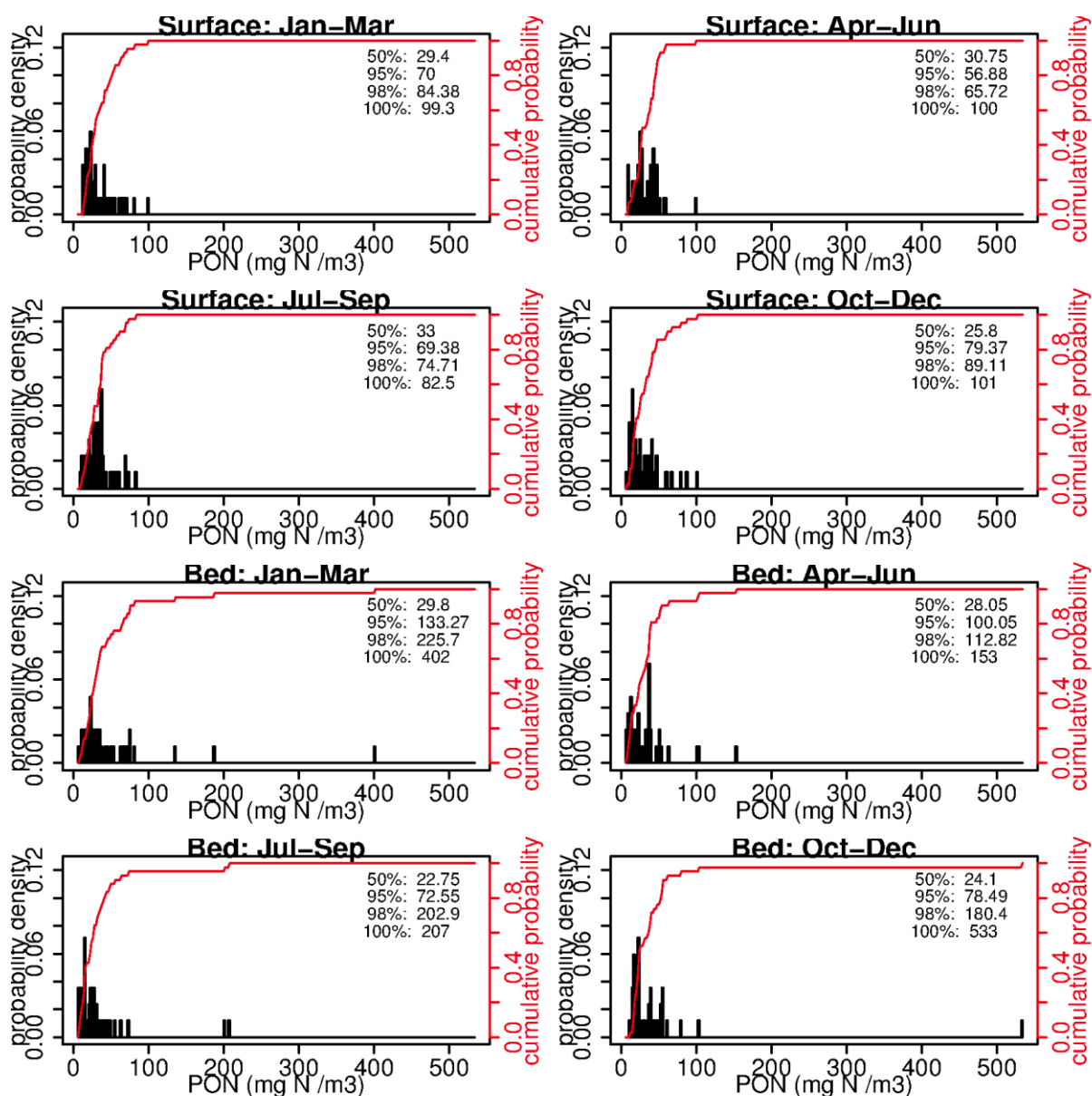


Figure C-11: Empirical probability density distributions for near-surface and near-bed particulate nitrogen (or particulate organic nitrogen in cases where that was measured instead) in Pelorus Sound.

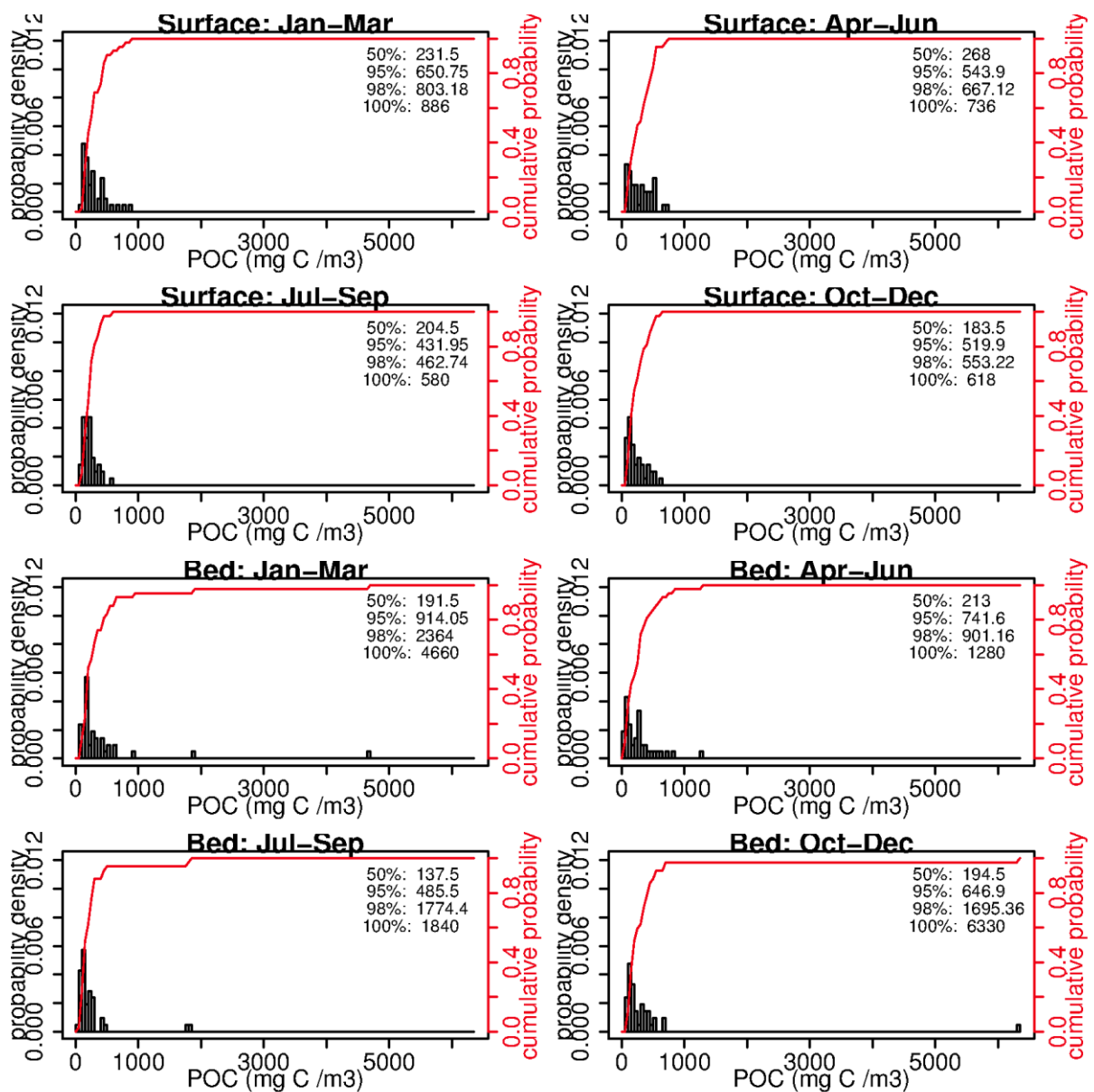


Figure C-12: Empirical probability density distributions for near-surface and near-bed particulate carbon (or particulate organic carbon where that was measured instead) in Pelorus Sound.

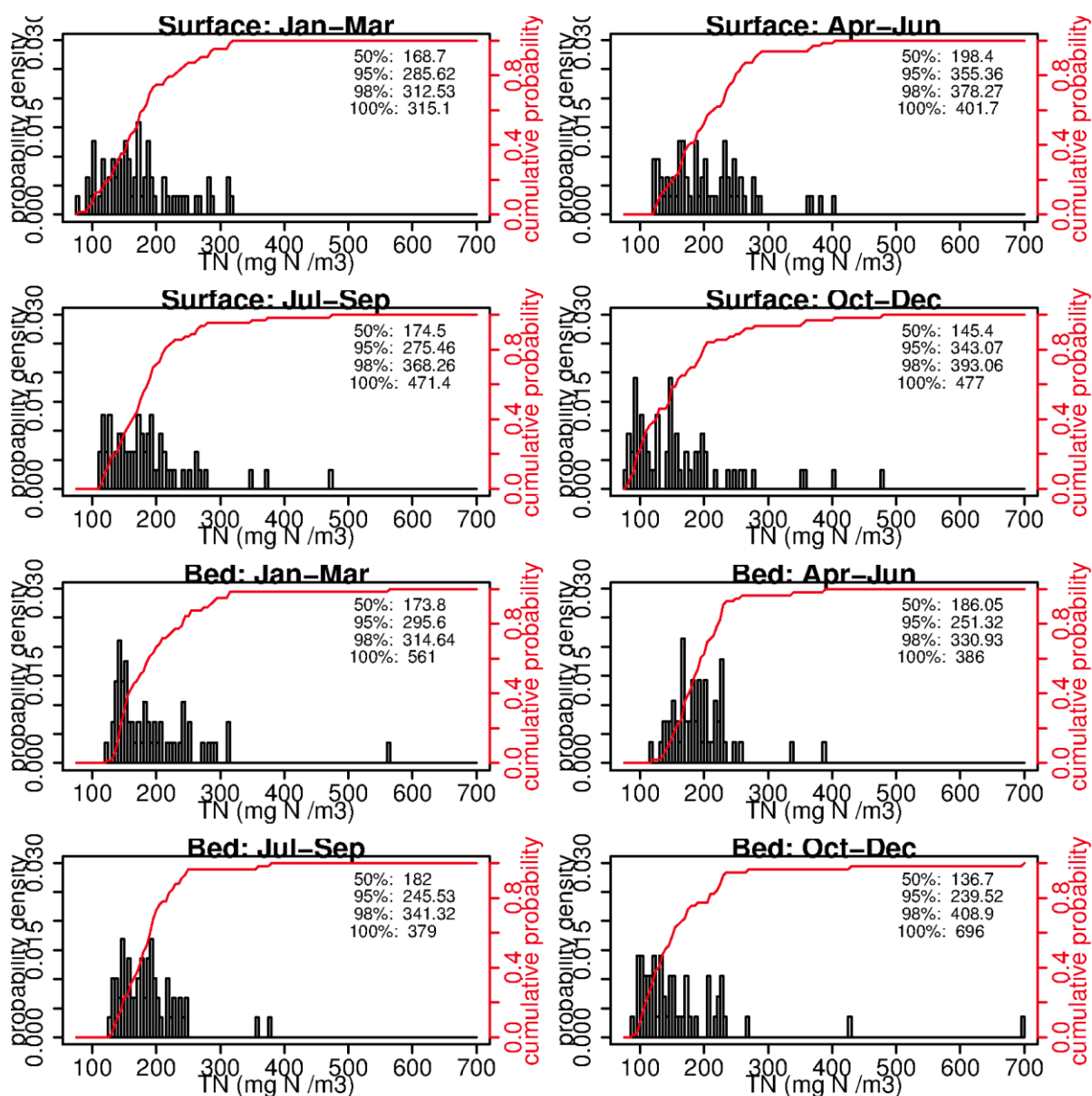


Figure C-13: Empirical probability density distributions for near-surface and near-bed total nitrogen in Pelorus Sound.

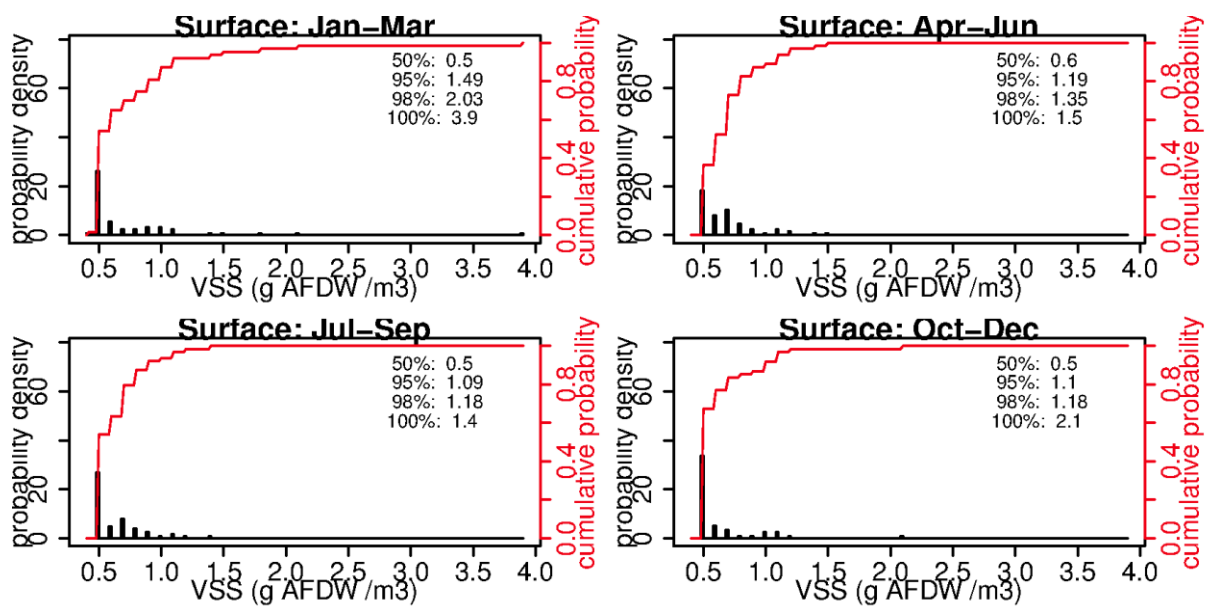


Figure C-14: Empirical probability density distributions for near-surface volatile suspended solids in Pelorus Sound.



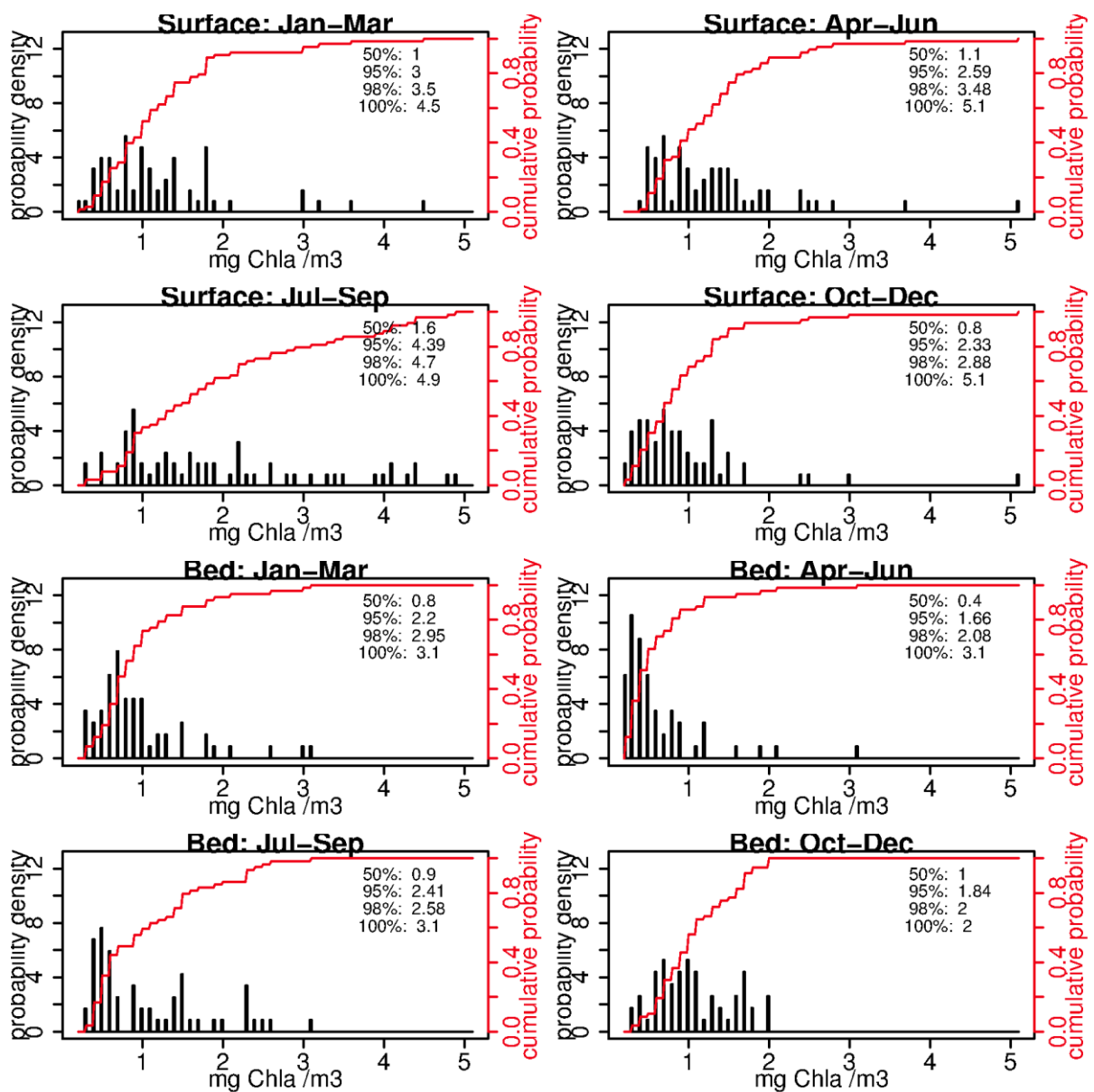


Figure C-15: Empirical probability density distributions for near-surface and near-bed chlorophyll concentration in Pelorus Sound.