Physical, Chemical and Biological Oceanographic Data Collected in Douglas Channel and the Approaches to Kitimat, June 2013-July 2014

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PHYSICAL, CHEMICAL AND BIOLOGICAL OCEANOGRAPHIC DATA COLLECTED IN DOUGLAS CHANNEL AND THE APPROACHES TO KITIMAT, JUNE 2013-JULY 2014

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ABSTRACT

Wright, C.A., Vagle, S., Hannah, C., and Johannessen, S.J. 2015. Physical, chemical and biological oceanographic data collected in Douglas Channel and the approaches to Kitimat, June 2013-July 2014. Can. Data. Report. Hydrog. Ocean.Sci. 196:viii+66pp.

Water, biological and sediment samples were collected in the Kitimat fjord system in July 2013 and April and July 2014 as part of a new, five-year baseline study. Instrumented moorings were deployed for a year at one site in Hecate Strait and two sites in Douglas Channel. Water samples were analyzed for dissolved oxygen, nutrients, salinity, dissolved inorganic carbon, alkalinity, dissolved organic carbon, coloured dissolved organic matter and oxygen stable isotopes. Instrument casts at the water sampling stations also measured profiles of temperature, salinity, oxygen, transmissivity and fluorescence. Suspended particles were collected at selected sites by filtration. The sediment grab samples were analyzed for organic carbon, total nitrogen, stable isotopes of carbon and nitrogen and mineralogical composition. A sediment core near the Hecate Strait mooring site was also analyzed for ^{210}Pb and ^{226}Ra for radio-dating, in addition to organic composition. Three Baker sediment traps deployed at each of two of the mooring sites collected a record of sinking particles at 50 m depth at 11.5 day intervals over July 2013 – June 2014. The moorings also included sensors to measure current, salinity, temperature, chlorophyll fluorescence and dissolved oxygen.

RÉSUMÉ

Wright, C.A., Vagle, S., Hannah, C., et Johannessen, S.J. 2015. Données océanographiques physiques, chimiques et biologiques recueillies dans le chenal Douglas et aux abords de Kitimat, de juin 2013 à juillet 2014. Rapp. stat. can. sur l'hydrogr. et les sci. océan. 196 : viii+66p.

Des échantillons d'eaux et de sédiments ainsi que des échantillons biologiques ont été recueillis dans le système de fjords de Kitimat en juillet 2013, de même qu'en avril et en juillet 2014, dans le cadre d'une nouvelle étude de base d'une durée cinq ans. Des amarrages équipés ont été installés pour une année à un site dans le détroit d'Hécate et à deux sites dans le chenal Douglas. Des échantillons d'eau ont été analysés afin de déterminer la concentration d'oxygène dissous, de nutriments, de carbone inorganique dissous, de carbone organique dissous, de matières organiques colorées dissoutes et d'isotopes stables d'oxygène, et déterminer la salinité et l'alcalinité. Les instruments installés aux stations d'échantillonnage de l'eau ont également mesuré les profils de la température, de la salinité, de l'oxygène, de la transmissivité et de la fluorescence. Les particules en suspension ont été recueillies par filtration à des sites sélectionnés. Les échantillons ponctuels de sédiments ont été analysés afin de déceler la présence de carbone organique, le contenu total en azote, la présence d'isotopes stables du carbone et de l'azote, ainsi que la composition minéralogique. On a également analysé une carotte

d'échantillonnage de sédiments recueillie près du site d'amarrage dans le détroit d'Hécate afin de détecter la présence de ^{210}Pb et de ^{226}Ra pour la datation radiométrique, en plus de déterminer la composition biologique. Trois pièges à sédiments Baker installés dans chacun des deux sites d'amarrages ont recueilli un nombre record de particules qui sombrent à une profondeur de 50 m, à 11,5 jours d'intervalle de juillet 2013 à juin 2014. Les amarrages comprenaient également des capteurs pour mesurer le courant, la salinité, la température, la fluorescence de la chlorophylle et l'oxygène dissous.

1.0 Introduction

The Kitimat fjord system on the northwest coast of Canada is the principal shipping route to the industrial town of Kitimat (Figure 1). Industries in Kitimat include an aluminum smelter and an international shipping port. There are plans for further industrial development including several proposed liquid natural gas plants and an oil pipeline with a terminus at Kitimat. The oil pipeline would carry diluted bitumen – a heavy tar mixed with light oils – from Alberta to Kitimat, after which it would be shipped by tanker through the fjord system to Hecate Strait and then across the Pacific Ocean to Asia.
In light of the potential increase in shipping, baseline physical, geochemical and biological data and time series were required for the Kitimat fjord system and Hecate Strait. In 2013 the Government of Canada launched a five-year programme to collect such data under the umbrella of the World Class Tanker Safety Programme. The goal of the observation program is to characterize the physical and chemical environment in order to 1) validate an ocean circulation model being developed; 2) provide advice on emergency response planning and habitat mapping; and 3) provide data for oil spill models. The scientific data collection for the World Class programme is being carried out by researchers from Fisheries and Oceans Canada, Natural Resources Canada, Environment Canada and the National Research Council.

This document reports physical, biological and geochemical data collected by Fisheries and Oceans Canada in the Kitimat fjord system and Hecate Strait during the first year of the programme (July 2013-June 2014). Sampling cruises took place in July 2013, April 2014 and June-July 2014. In addition, three moorings were deployed, one in Hecate Strait and two in Douglas Channel. Depth profiles of temperature, salinity, transmissivity, fluorescence, PAR, and dissolved oxygen were measured, while bottle samples were collected for the analysis of dissolved oxygen, salinity, nutrients, and, in some locations, dissolved inorganic carbon, alkalinity, dissolved organic carbon, coloured dissolved organic matter and oxygen stable isotopes. Phytoplankton and zooplankton were also collected.

Suspended particles were collected by filtration at selected sites during the 2014 cruises. A sediment core was taken in Hecate Strait and sediment grab samples were collected at six of the rosette stations and analyzed for organic and inorganic composition. The moorings included a set of Baker sequential sediment traps at 50 m depth to collect sinking particles, as well as electronic sensors to measure current, salinity, temperature, chlorophyll fluorescence, turbidity and oxygen. The data are tabulated and / or plotted in this report and are available electronically on request from the IOS data archive (http://www-sci.pac.dfo-mpo.gc.ca/osap/data/default_e.htm) or from the authors. A companion Technical Report, Johannessen *et al.* (2015), interprets the first year of geochemical data in the context of seasonality and physical circulation.

2.0 Methods and Results

2.1 Mooring Design and Sampling

Figure 1 shows the location of moorings in the study area (HEC1, FOC1, and KSK1). The moorings had various combinations of current meters, CTDs and ADCPs (Figure 2). Sampling intervals varied among the instruments to balance sampling rate. Moored sensor data are shown in Figures 3-5.

Two moorings (HEC1 and FOC1) contained three Baker sediment traps which were accompanied by a current meter and CTD (SBE19p) with a Wetlabs ECO-FLNTU. The Baker traps are described by Baker and Milburn (1983) and O'Brien *et al* (2000). For each 1 L of 0.2 µm filtered seawater (initial salinity ~30-31 reported on the Practical Salinity Scale) 11g of ultrapure NaCl was added to provide a brine stock for traps (final salinity 38-40). To each cup, 2.36 ml of saturated mercuric chloride solution was added and the solution topped up with the brine for a total volume of ~175 ml (approximate final concentration 1 mg/ml). This provides an environment where bacterial growth and subsequent chemical alterations to the particulates are inhibited. Each sediment trap contains 10 sampling cups for a total of 30 cups throughout the year with a sampling interval of 11.5 days. Traps were configured such that when one trap (cup 10) was completed, the next sequential trap would begin to collect.

Handling and analytical analysis for sediment trap samples for total mass, total carbon, organic carbon, nitrogen and carbonate analysis are described as per sediment methods cited in section 2.7 and also O'Brien *et al*. (2000) and Wright *et al.* (2007). Results are shown in Table 1.

2.2 Water Property Sampling

A SBE911 CTD + 24-bottle rosette was deployed along a series of stations to characterize the water column for primary variables (temperature, salinity (as conductivity) dissolved oxygen (SBE43), chlorophyll fluorescence (Seapoint and Wetlabs), transmissivity (Wetlabs C-Star) and photosynthetically-active radiation (400-700nm, PAR, Biospherical). CTD data are collected in both the downcast and upcast phase, but only downcast data is used for sensor characterization of the water column while the upcast is used to characterize conditions during niskin tripping. The SBE911 samples 24 scans per second with the number of scans averaged equalling 1. Stations varied from cruise to cruise along the same transect (established during cruise 2013-50, see Figure 6).

The CTD was allowed to equilibrate/pump on the surface (~0.5-1 m for a minimum of 30 seconds) before descending at a rate of 1m s^{-1}. As we wish to characterize the surface waters (1-10 m) we do not do this equilibration at 10m and return to surface, since this would disturb those waters. CTD profiles are also critical for quality control/assurance of the moored sensors to assess possible drift/offset.

The 10 L niksin bottles were fired at standard depths on the upcast. Bottles were allowed to equilibrate for a minimum of 30 seconds at each depth prior to firing.

At four stations (HEC1, SC61, FOC1 and Doug4) 2 bottles were fired at each depth in order to allow extensive sampling for expanded chemical analysis. At all other stations, the expanded chemistry were only performed on the surface bottles. Samples were collected for: dissolved oxygen (Winkler); nutrients (nitrate + nitrite, silicate, soluble orthophosphate), dissolved inorganic carbon/alkalinity (DIC/Alk), salinity, colour dissolved organic matter (CDOM), dissolved organic carbon (DOC), total organic carbon (TOC), oxygen isotopes ($\delta^{18}O$), extracted chlorophyll (surface, 10 m and 20 m only), and phytoplankton (selected stations). A salinity sample was also taken from each bottle (data not shown) for conductivity cell calibration on the SBE9 and for certain bottle-derived analyses where the corresponding sample salinity is required for the determination of the variable (e.g. DIC/Alk) or if it has relevance to another variable (e.g. oxygen isotopes, CDOM).

CTD data are post-processed at the Institute of Ocean Sciences (IOS) using standard routines to correct for thermal mass, hysteresis, and descent issues. Data is de-spiked, filtered, and bad data removed or flagged. Data is corrected using calibrations, knowledge of sensor history and also against long-term climatology for any errors that might be from sensor drift. As sensor dissolved oxygen is a derived value, the sensor is checked against samples taken for Winkler analysis and possible corrections to bottle firing depth are considered. Finally, data are binned to 1 m averages. All CTD data (raw, partially processed and final product) are archived at IOS.

The data from the down-cast analysis are shown in Figures 6-7; 9-13; and 15-16. All station maps and data have been plotted in Ocean Data View (Schlitzer, R., 2008).

2.3 Chemical Analysis

Dissolved oxygen samples (data not shown) were analyzed at sea on an automated Winkler titration system. (Brinkmann Dosimat model 665 for titrations, Dosimat model 865 for dispensing standards and a PC950 Colorimeter controlled by AutoOxy software V3.4) with modifications based on Carpenter (1965) and adhering to WOCE protocols (Culberson 1991).

Nutrient samples were collected in plastic tubes and quick-frozen in aluminum blocks stored at -20 °C. All samples were returned to IOS for analysis. They were analyzed using an Astoria analyzer following methods described by Barwell-Clarke and Whitney (1996).

Chlorophyll samples were taken from the niskins and immediately were filtered onto 25 mm GF/F filters and stored in glass scintillation vials at -20°C prior to analysis. Samples were extracted in 90% acetone at -20°C for 24 hours in the lab and analyzed on a Turner 10AU fluorometer calibrated with commercially pure chlorophyll *a* (Sigma). Fluorescence readings taken before and after acidification were used to calculate chlorophyll (Holm-Hansen *et al.* 1965). The average of two samples is reported.

Salinity samples were collected in 200 mL type ll glass bottles with disposable plastic inserts and screw caps supplied by Ocean Scientific International Limited. They were analyzed in a temperature-controlled lab on a Guildline 8400B Salinometer standardized with IAPSO standard seawater . Samples were stored <1 month prior to analysis.

Samples collected for DIC/Alkalinity were treated with 100 µl of saturated mercuric chloride to inhibit bacterial growth/activity. Samples were stored under cold conditions prior to analysis back at IOS. Analysis follows the Standard Operating Procedures as described in Dickson *et al*. 2007, SOP 2 and 3B.

Scintillation vials (40 ml) with a 0.125 cm Teflon low bleed septum were cleaned in Extran 300 and rinsed several times with Type I Ultrapure water. Vials were then soaked in 10% HCl for a minimum of four hours and rinsed several times with Type I Ultrapure water. They were then allowed to dry and were baked at 450 °C for a minimum of 5 hours. Septa were briefly washed in 10% HCl, rinsed with Type I Ultrapure water and allowed to air dry. These vials were used in the collection of DOC and TOC. TOC was collected directly from the niskin spigot while the DOC samples were water was passed through a Millipore Opticap XL Durapore 0.22 µm inline filter cartridge (Product No. KVGLA04HH3) attached to the spigot. Vials were then frozen at -20°C. At the time of writing this report, the TOC and DOC samples have not been analyzed. The analysis will take place on a Schmiadzu TOC-L following SOP 7 of Dickson *et al*. (2007) with some expected modifications due to the use of different acids and sparging times.

Water was passed through a Millipore Opticap XL Durapore 0.22 µm inline filter cartridge (Product No. KVGLA04HH3) into a 125 ml amber bottle for CDOM analysis. Samples were refrigerated and returned to IOS. Spectral absorbance (280-700 nm at 1nm resolution) was measured with a HP Agilent 4853 spectrophotometer. Data were then corrected for instrument offset and the slope and absorbance at 350nm (magnitude) were determined using a curvilinear best of fit for 280-550nm curve (See Johannessen *et al*., 2007 and Stedmon *et al.*, 2000). The instrument offset accounts for temperature, refractive index differences between the sample and the blank (Type II water), as well as for scattering.

Oxygen isotope samples were collected directly from the niskin spigot into 30ml plastic (PETG or PP) bottles, the cap secured with parafilm, and refrigerated. The samples were then shipped to the G. G. Hatch Stable Isotope Laboratory at the University of Ottawa for analysis. The analysis were performed on an Isotope Ratio Mass Spectrometer (IRMS) Delta Plus XP (Thermo, Germany) interfaced with a GasBench II. 0.6 mL was pipetted into an Exetainer. Samples and internal standards are flushed with a gas mixture of 2% CO_2 in helium off-line. Exetainers are left to equilibrate at either 25 °C or simply room temperature for >5 days.

The data is reported in Delta notation δ, the units are per mil (‰) and defined as $\delta = ((Rx-Rstd))/Rstd)*1000$ where R is the ratio of the abundance of the heavy to the light

isotope. reported as ‰ vs. VSMOW and normalized to internal standards calibrated to International standards VSMOW (0,0), GISP(-24,8, -189,5) and SLAP (-55,5, -428.0).

Precision is evaluated by including in every sequence a reference water standard, known as W-20. The values of this water are used for long term monitoring and statistical purposes. W-20 is reported as the average of the measured values, n and the standard deviation of the sequence. Generally, a sequence run holds 65 samples, and includes 4 sets of internal standards (known as W-7,9,10) and 4 blind standards (W-20) and the standard deviation of W-20 is less than 0.15 for oxygen. Random duplicates of a sample are also run.

The data from the up-cast bottle sample analysis are shown in Figures 8, 14, and 17.

2.4 Underway CTD (UCTD) data

The Underway CTD (UCTD) profiling system was developed to obtain high quality conductivity and temperature data as functions of depth without the use of complex and expensive profilers (Vagle *et al*. 2013). The system was introduced in 2008 and developed by The Oceanscience Group (San Diego, USA), and using a special CTD probe developed by SeaBird Electronics Ltd. (Bellevue, USA).

Between April 14-17, UCTD casts were completed in Ursula Channel and into Princess Royal Channel (Figure 18A). The composite transects of temperature and salinity collected by profiling on April 17th are shown in Figure 19.

The system was used in a continuous operating mode along 4 transects across the sill in Verney Passage (Figure 18B) between 0718 and 1115 (PDT) on 17 April. During these transects the probe was set to operate continuously and was equipped with a foam collar to reduce the drop speed to approximately 2 m/s. The pressure record with corresponding temperature and salinity for one of these transects is shown in Figure 20.

2.5 Acoustic Doppler Current Profiler (ADCP) data

A Teledyne RD Instruments Workhorse Sentinel Acoustic Doppler Current Profiler (ADCP) was mounted on a steel pole deployed over the side of the ship during the transects across the Verney Passage sill to measure acoustic backscatter from bubbles and zooplankton and to estimate horizontal and vertical currents along the tracks. The instrument was deployed from 22:38 (PDT) 16 April to 11:15 17 April 2014 and operated at 307.2 kHz, with 81 1m bins, the first bin 2.2 m below the instrument, or approximately 4 m below the sea surface. The system was set to use 1 ping per ensemble, with approximately 0.5 pings per second. An example of the 307 kHz backscatter across one of these transects across the sill is shown in Figure 21.

2.6 Moving Vessel Profiler (MVP) data

A Rolls-Royce Moving Vessel Profiler (Type-200 MVP) was deployed to obtain high resolution temperature and salinity profiles while the ship was underway The MVP system consists of temperature, conductivity and pressure sensors housed in a small,

streamlined free fall fish, a conductor cable with strength member, a computer-controlled high speed hydraulic winch and a complete cable metering, overboarding and docking system. The MVP allows the free fall fish to fall near-vertically. Deployment is executed under computer control and can be restrained by one of three parameters: desired depth of cast, preset height above the bottom or maximum cable out. Once the programmed downcast depth was reached, the fish was towed near the surface where it was recovered and re-deployed.

The MVP was deployed in Princess Royal Channel at 1444 (PDT) 14 April 2014, while the ship was steaming north at 8 knots. The system was operated for four hours until 1826. The locations of the resulting 40 profiles are shown in Figure 18B. Contour plots of temperature and salinity from these profiles, augmented with UCTD and CTD profiles from the start of the MVP run and northward to Kitimat in Douglas Channel are shown in Figure 22.

2.7 Sediment and Particulate Sampling

A sediment core was taken at HEC1 during the 2013-50 cruise using a Pouliet Box Corer The core was sectioned in the shipboard laboratory into 1 cm intervals for the uppermost 10 cm, 2 cm intervals for the next 10 cm and 5 cm intervals for the remainder of the core (20 cm to bottom; ~ 40 cm). Sediment consisted primarily of sandy mud. Core sections were homogenized then subsampled for organic carbon, carbonate carbon, total nitrogen and the stable isotopes of carbon and nitrogen.

A subsample of each sediment core depth interval was sent to Flett Research Ltd. in Winnipeg, Canada for analysis of ^{210}Pb and ^{226}Ra to be used for radio-dating. ^{210}Pb was measured in all sections of each core following the procedure of Eakins and Morrison (1978), in which the activity of ^{210}Pb is inferred from that of ^{210}Po (counting errors < 6%). The activity of supported ^{210}Pb was determined as the average of the ^{226}Ra activity measured at three depths (top, middle, bottom) in each core, from the ingrowth of ^{222}Rn over at least 4 days following Mathieau *et al.* (1988) with modifications by Flett Research Ltd.

Sediment grabs were collected along Douglas Channel (see Figure 6) for mineralogy, and elemental/isotopic composition were collected using a 0.1 m^2 Smyth Macintyre grab. Samples were put into 50ml plastic centrifuge vials and then frozen at -20 °C. Carbon and nitrogen were analysed at the University of British Columbia using the method of Calvert *et al.* (1995), in which organic carbon is calculated as the difference between total and carbonate carbon. Total carbon is measured by combustion and gas chromatography in a CHS analyzer (Carlo-Erba) and carbonate carbon by coulometry (precision ± 1.6%, 1 standard deviation). Stable isotopes of carbon and nitrogen were measured using Calvert *et. al.* (2001). Isotopes of carbon and nitrogen were measured at the DeltaPlus Laboratory at the University of British Columbia and follows Calvert *et al*. (2001). Data are shown in Table 2.

Mineralogy samples, measured at the University of British Columbia by x-ray diffraction, were reduced to the optimum grain-size range for quantitative X-ray analysis (<10 μm) by grinding under ethanol in a vibratory McCrone Micronizing Mill for 7 minutes. Continuous-scan X-ray powder-diffraction data were collected over a range 3-80°2θ with CoKa radiation on a Bruker D8 Advance Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffracted-beam Soller slits and a LynxEye-XE detector. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°.

The X-ray diffractograms were analyzed using the International Centre for Diffraction Database PDF-4 using Search-Match software by Bruker. X-ray powder-diffraction data of the samples were refined with Rietveld program Topas 4.2 (Bruker AXS). The Rietveld refinement plots are shown in Table 3.

Suspended particle concentrations were measured in water samples collected during the two 2014 cruises (see station locations from Figures12 and 15). Collection of water was either directly from the surface 1.7 L niskin or from a bucket thrown from the ship. A minimum of 3L of water were filtered through three sequential filters; GF/C (1.2µm), then GF/F (0.7µm) and then 0.2µm nucleopore. Filters were then frozen at -20 °C until returned to IOS. Filters were dried to a continuous weight at 50°C in a drying oven and then weighed on a Toledo Mettler balance to 0.0001 g. Weights were divided by volume filtered to determine suspended particle concentration (SPC) in mg L^{-1} (Table 4).

For loss on ignition (LOI) to determine the percent organic matter of the particles, the GF/C and GF/F filters were baked at 450°C for a minimum of 5 hours, cooled and reweighed. Results for LOI are shown in Table 5.

Just prior to water sample collection, turbidity of the surface water was measured with a, a SBE25 CTD + Seapoint turbidity sensor. The raw voltage was used to characterize the relative SPC rather than the derived variable because derived turbidity values are affected by not only relative particle concentrations, but also particle types, size and behaviours in water masses (Table 4).

2.8 Biological Sampling

Phytoplankton samples (~200 ml) were collected from the surface niskin of the main rosette system, into amber glass jars that contained a saturated Lugol's Acid Iodine solution (Throndsen, 1978). Samples were swirled to mix and then a 25 ml subsample was settled using a sliding chamber system from Hydro-Bios. A minimum of 100 dominant and 300 total cells were counted or, a maximum of 3 transects using a Zeiss inverted phase contrast microscope. Results of the analysis, including scan type and magnification factors are shown in Tables 6-7.

Zooplankton samples were collected by vertical haul using a SCOR plankton net (236 µm) with a TSK flowmeter. The net was lowered to a selected depth at 0.5m s^{-1} and retrieved at 1.0 m s^{-1}. Samples were then fixed in 10% formalin/seawater and returned to IOS for identification and counts. Taxonomic classification, counts and metrics are

reported as per Mackas (1992). Results of the analysis are shown in Tables 8-9. Appendix I provides the nomenclature key used at IOS.

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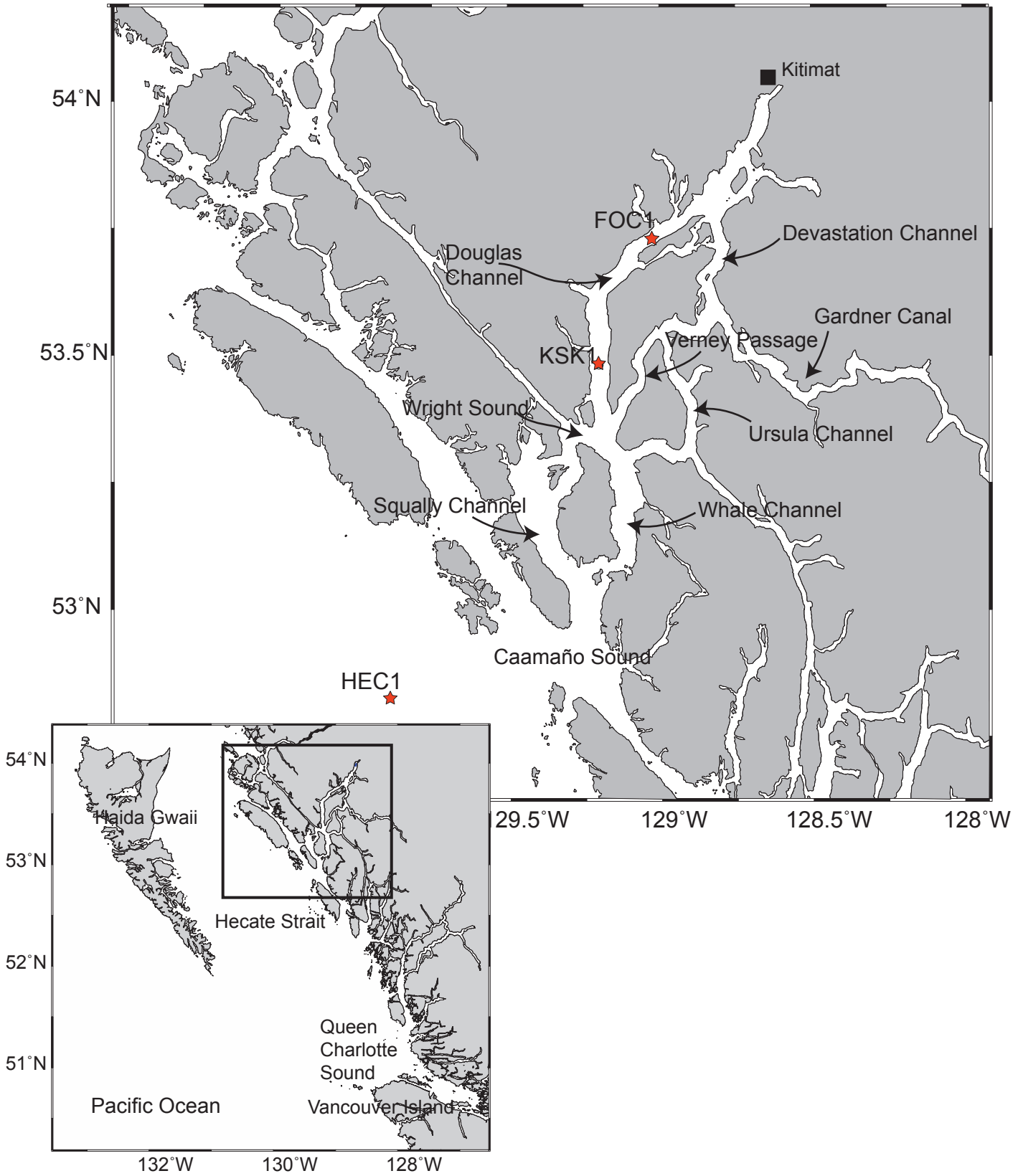

Figure 1. Principle region of study and mooring locations in Douglas Channel and Hecate Strait as part of the World Class Tanker Safety Program, Phase 1: July 2013-June 2014.

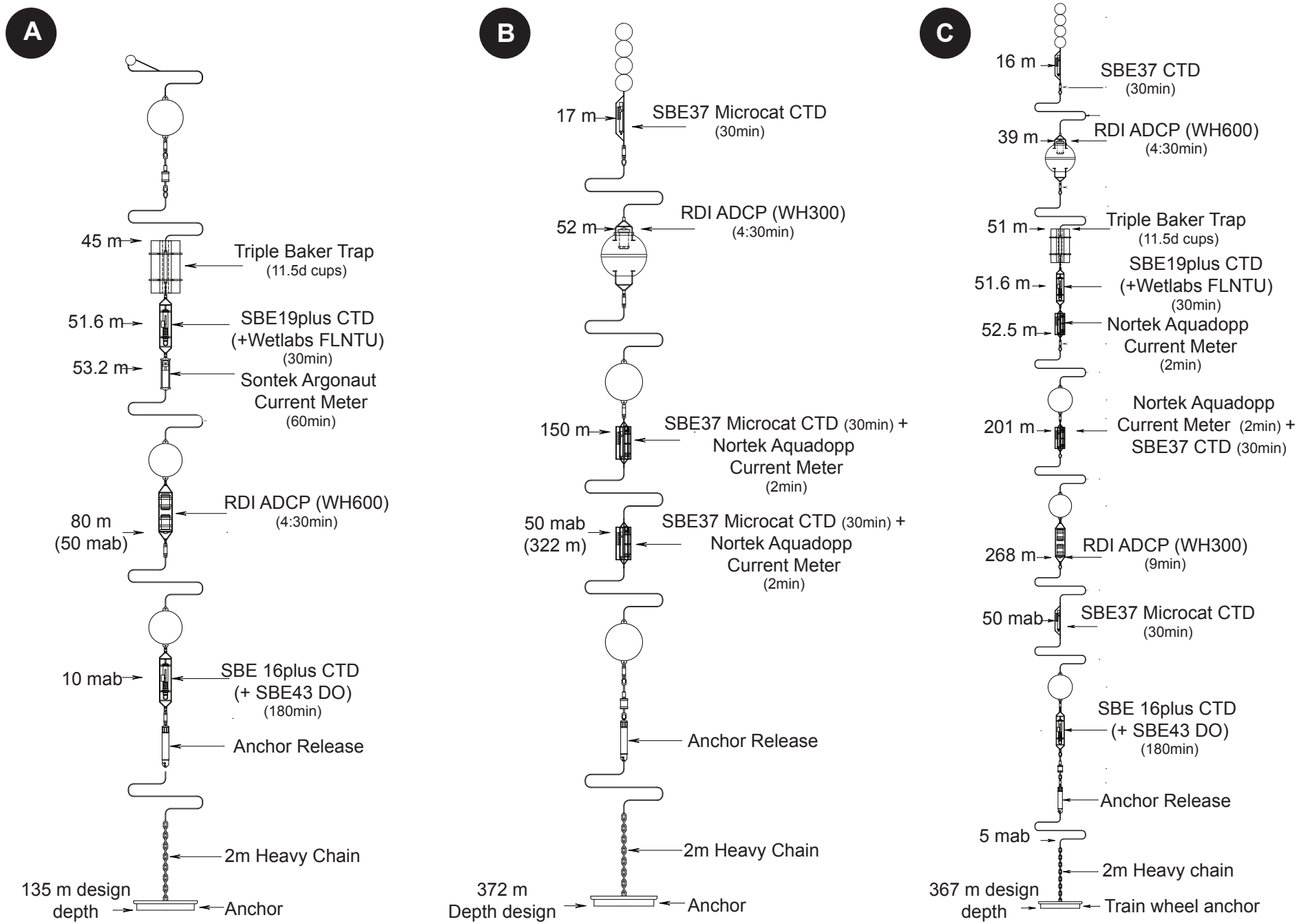

Figure 2. Mooring schematic, including sampling frequency for moorings A) HEC1; B) KSK1; and C) FOC1. mab=metres off bottom; d= days; min=minutes.

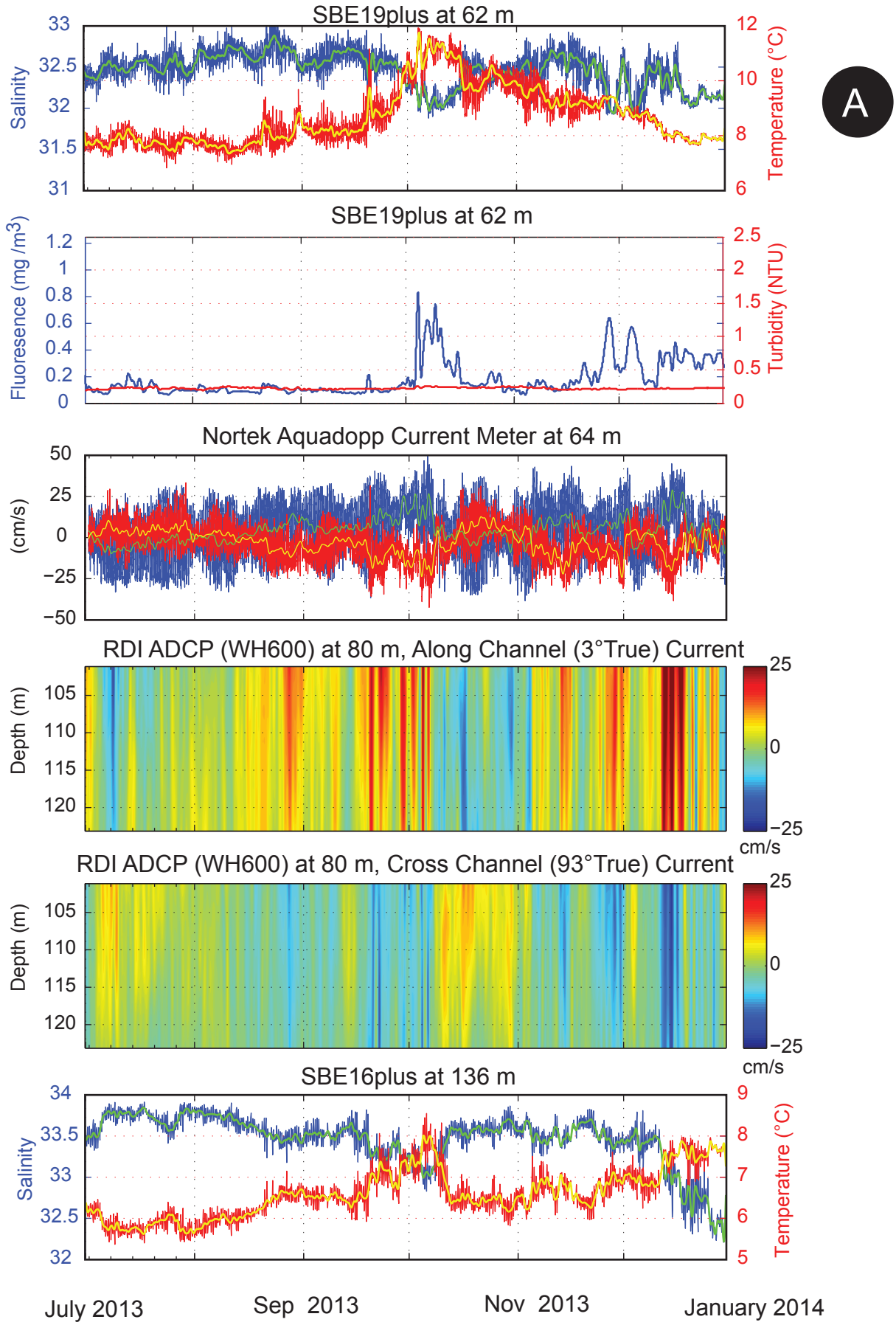

Figure 3. Data composites for instrumentation moored at HEC1. Panel A: August to December, 2013. Panel B: January-June, 2014. Lines through plotted raw data represent the 30 hour filter values.

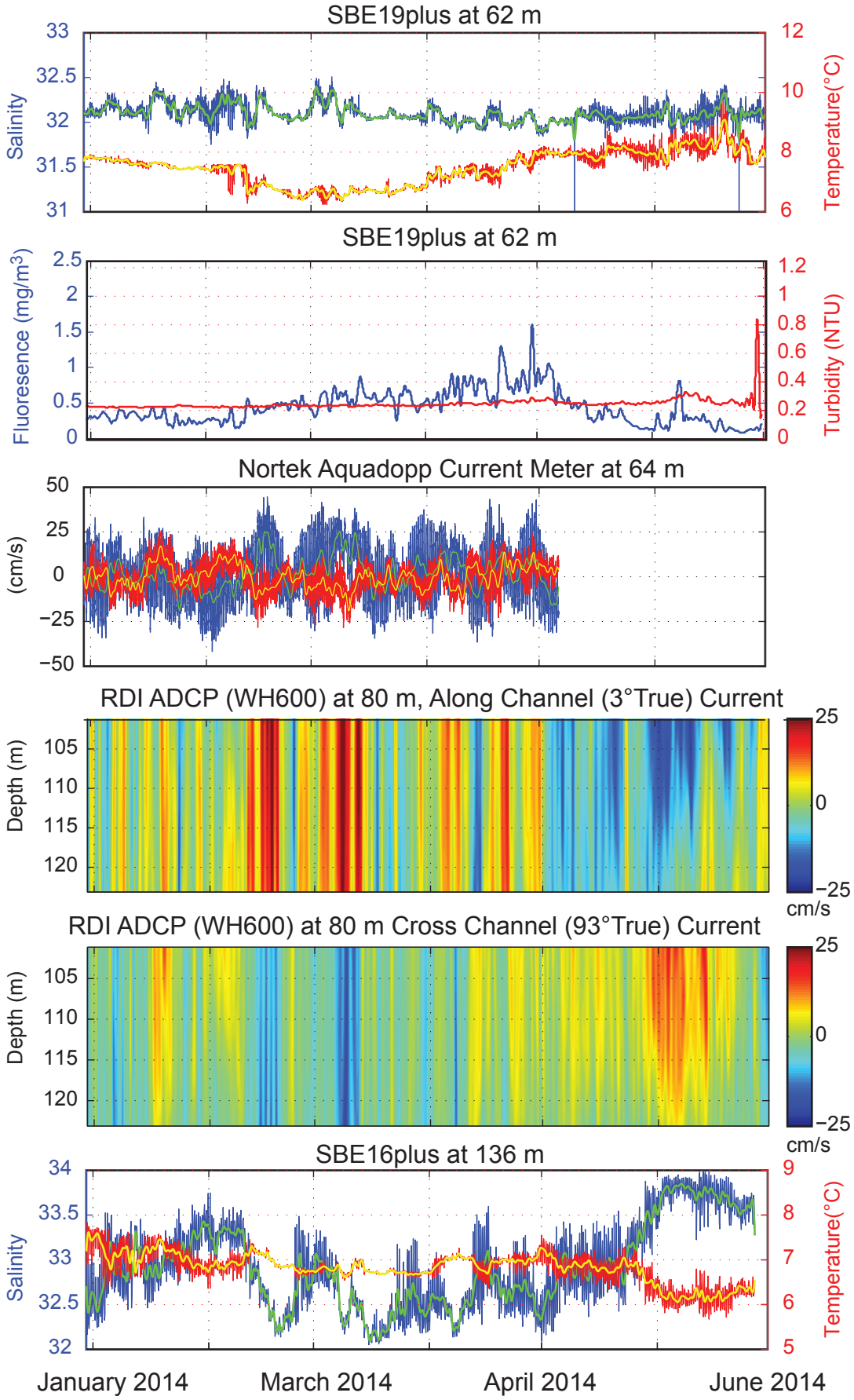

Figure 3 continued. Data composites for instrumentation moored at HEC1. Panel A: August to December, 2013. Panel B: January-June, 2014. Lines through plotted raw data represent the 30 hour filter values.

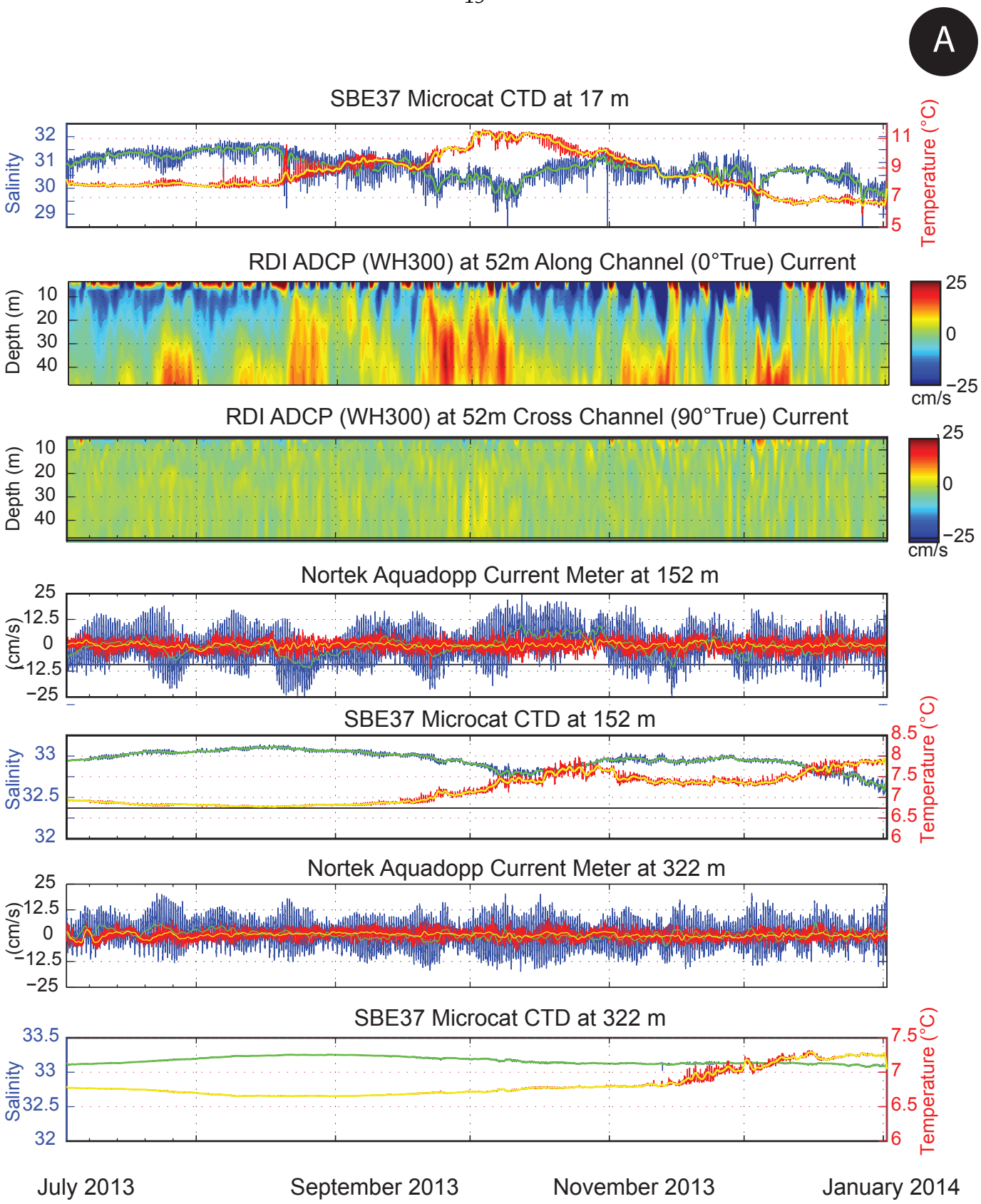

Figure 4. Data composites for instrumentation moored at KSK1. Panel A: August to December, 2013. Panel B: January-June, 2014. Lines through plotted raw data represent the 30 hour filter values.

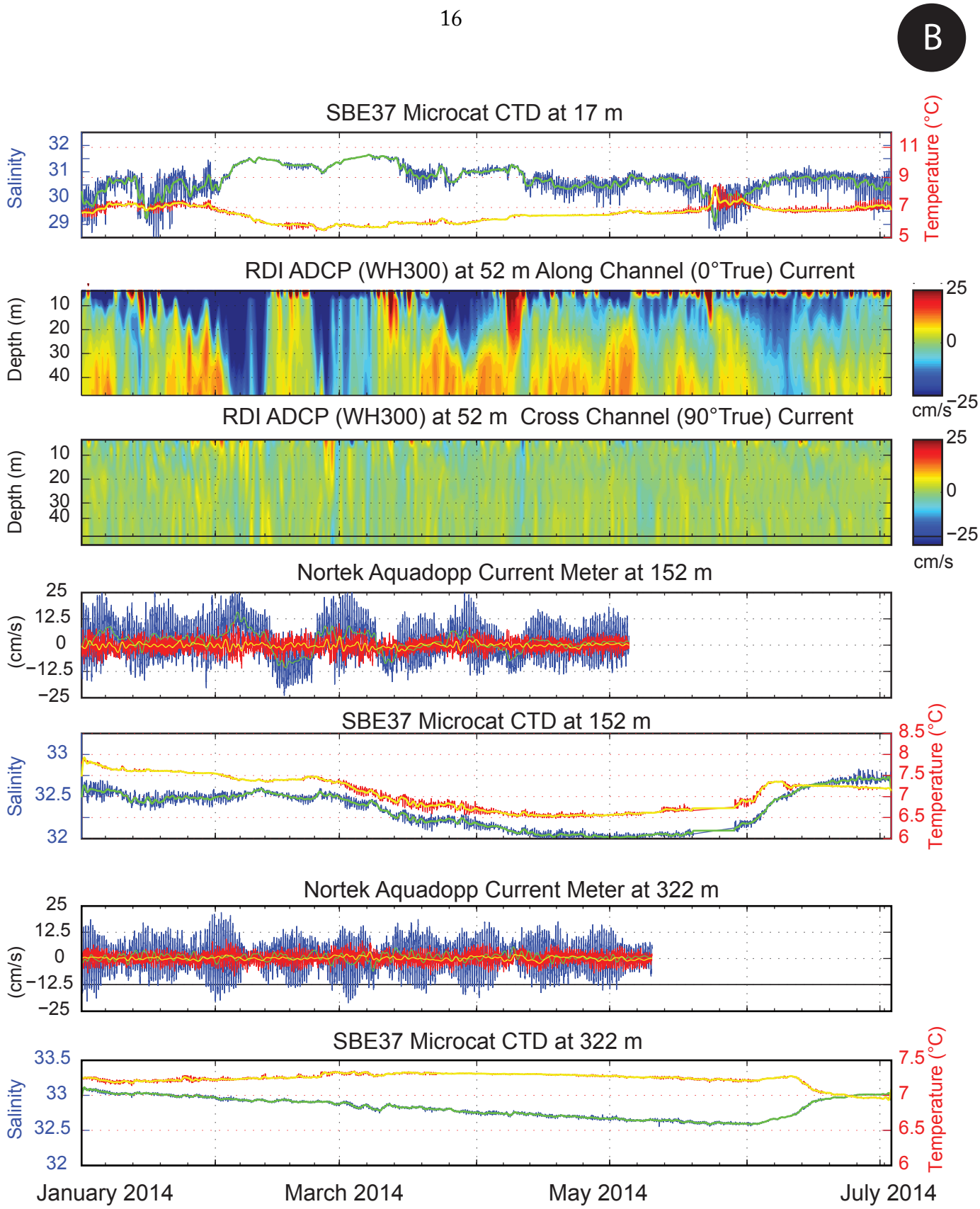

Figure 4 continued. Data composites for instrumentation moored at KSK1. Panel A: August to December, 2013. Panel B: January-June, 2014. Lines through plotted raw data represent the 30 hour filter values.