

Kwang-Hun Lee¹, Shahid Ali¹, Yena Kim¹, Kitack Lee^{2,3}, Sae Yun Kwon^{1,2,3}, and Jonghun Kam^{1,2,3}

¹Division of Environmental Science and Engineering, Pohang University of Science and Technology

²Institute for Convergence Research and Education in Advance Technology, Yonsei University

³Pohang University of Science and Technology

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Abstract

Reliable nutrient load estimation of a reservoir is challenging due to inconsistent spatial extent and temporal frequency of water quality and quantity. This study aims to collect consistent spatial extent and temporal frequency of water depths and nitrate concentrations of a reservoir in South Korea using uncrewed surface vehicle (USV). In this study, reservoir nitrate loads were estimated using four methods to examine how spatial variation in water depth and nitrate concentrations affected load estimates. Based on dual measurements of water depth and nitrate concentration, reservoir nitrate loads across 30 sampling dates (0.7 million tons of fresh water on average) ranged from one to four tons. Results showed that a point measurement of water depths and nitrate concentrations can cause up to -17% of underestimation of nitrate loads, particularly after intense rainfall events. This study highlights potential opportunities and challenges of the USV-based dual monitoring systems for water quality and quantity.

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High Resolution Mapping of Nitrate Loads of a Reservoir Using an Uncrewed Surface Vehicle:
Potential opportunities and Challenges

Kwang-Hun Lee¹, Shahid Ali¹, Yena Kim¹, Kitack Lee^{1,2}, Sae Yun Kwon^{1,2}, Jonghun Kam^{1,2*}

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¹Division of Environmental Science and Engineering, Pohang University of Science and
Technology, Pohang, South Korea

²Institute for Convergence Research and Education in Advance Technology, Yonsei University,
Seoul, South Korea

*Corresponding author:
Dr. Jonghun Kam (jhkam@postech.ac.kr)
Division of Environmental Science and Engineering
Pohang University of Science and Technology
Pohang, South Korea 37673
Phone: +82-54-279-2318
Fax: +82-54-279-8299

Key Points:

- An uncrewed surface vehicle (USV) was used to map water depth and nitrate concentration at a 10-meter resolution.
- Nutrient load estimates varied up to 17% when comparing the USV method to a point-measurement method.
- Limitations and challenges of USV-based surveys for water quantity and quality were discussed.

34 **Abstract**

35 Reliable nutrient load estimation of a reservoir is challenging due to inconsistent spatial
36 extent and temporal frequency of water quality and quantity. This study aims to collect
37 consistent spatial extent and temporal frequency of water depths and nitrate concentrations of a
38 reservoir in South Korea using uncrewed surface vehicle (USV). In this study, reservoir nitrate
39 loads were estimated using four methods to examine how spatial variation in water depth and
40 nitrate concentrations affected load estimates. Based on dual measurements of water depth and
41 nitrate concentration, reservoir nitrate loads across 30 sampling dates (0.7 million tons of fresh
42 water on average) ranged from one to four tons. Results showed that a point measurement of
43 water depths and nitrate concentrations can cause up to –17% of underestimation of nitrate loads,
44 particularly after intense rainfall events. This study highlights potential opportunities and
45 challenges of the USV-based dual monitoring systems for water quality and quantity.

46 **Plain Language Summary**

47 Water quantity and quality are monitored at different spatial extent and temporal
48 frequency. This study used an uncrewed boat to measure the water depth and nitrate
49 concentration of a reservoir in the mid-eastern Korean Peninsula at considering the spatial
50 component and temporal components. This uncrewed boat was equipped with water depth and
51 nitrate concentration sensors. During the study period (2021–2022), uncrewed boats conducted
52 30 surveys. We found strong seasonal variations in nitrate load estimates in the reservoir,
53 particularly during the wet season. These results suggest that estimating nitrate loads from depth
54 measurements at a point measurement in a reservoir can lead to underestimates. This study is a
55 case study how the cutting-edge technologies like our uncrewed boat equipped with
56 environmental sensors can be used for the next-generation water monitoring system.

58 **1. Introduction**

59 Nitrate is derived from natural and anthropogenic inputs via nutrient deposition from the
60 atmosphere (Kim et al., 2011; Kim et al., 2014; Liu et al., 2013). Lakes and reservoirs have been
61 used to monitor changes in inland nitrate deposition, which can affect their aquatic ecosystems
62 (Elser et al. 2009). Such a nutrient regime shift in lakes and reservoirs via atmospheric
63 deposition may change the structure of aquatic ecosystems and threaten the biodiversity (Folke et
64 al., 2004). The water depth or water storage volume of a reservoir can affect water quality and is
65 controlled by precipitation and water usage. Water quantity and quality of reservoirs are strongly
66 associated with each other, particularly during the wet/dry season (Larsen et al., 1999).
67 Monitoring changes in water depth and nitrate concentration of lakes and reservoirs requires a
68 holistic monitoring system of hydroclimatological variables including precipitation, temperature,
69 and biogeochemical transformations (e.g., assimilation and denitrification; Kendall et al., 2007;
70 Pellerin et al., 2014).

71 Strong seasonality has been often reported in the water depth, water storage volume,
72 shape, size, and ecology of a reservoir, which can affect nutrient mixing process and may lead to
73 harmful algal blooms (Feyisa et al., 2014; Pekel et al., 2016). Hydroclimatic extremes, such as
74 droughts and floods, can show clear interactions of water quality and quantity. A severe drought
75 increases the nitrate concentration and the hydraulic residence time in the aquatic system
76 (Beklioglu et al., 2008). As air temperature increases and long hydraulic residence time, water
77 temperature also increase enhancing stratification in freshwater systems. (Baldwin et al., 2008).
78 This may lead to toxic cyanobacterial blooms and lowered dissolved oxygen concentrations

79 (Chapra, 1997). Reduced flushing and enhanced productivity also elevate nutrient, turbidity and
80 algal levels (Mosley, 2015). This environment can trigger eutrophication and cause catastrophic
81 impacts on the aquatic ecosystem (Zhang et al., 2018). Heavy rainfall increases surface runoff
82 and non-point pollutant transports from the surrounding areas of the reservoir into the aquatic
83 systems (Golladay et al., 2002). Furthermore, environmental incidents can degrade significantly
84 the water quality, causing a lack of available water resources and increasing negative complaints
85 regardless of the amount of water resources (Liu et al., 2023). While degraded water quality may
86 restrict availability for certain purposes, such as recreational activities, it may still be suitable for
87 other critical applications like flood control (Cao et al., 2021). Therefore, both water quality and
88 quantity indices can help monitor the availability of water resources accurately with spatially and
89 temporally consistent measurement of water quantity (Yu et al., 2016), which is crucial for
90 proactive management of water resources (Cao et al., 2021).

91 Water quantity and quality have been monitored at inconsistent sampling frequencies
92 and site locations worldwide. For example, the water level of a reservoir is measured hourly, and
93 the water quality is monitored at weekly or longer. These different sampling frequencies of water
94 quality and quantity of the reservoir are a potential source of uncertainties in assessing the
95 availability of water resources (water quantity: Faro et al., 2019; Gosling and Arnell, 2016; Luo
96 et al., 2020; water quality: Al-Omran et al., 2015; Schoumans et al., 2014; Reynolds et al., 2016;
97 Cassidy and Jordan., 2011). Over the last decade, new technologies have been implemented for
98 efficient water quality monitoring and bathymetric surveys. A low-cost probe with multiple
99 electrochemical sensors can monitor water quality parameters at once in real time. The field
100 deployment of this multiple parameter probe at a gauge site showed acceptable agreement in
101 temperature, specific conductance, pH, and DO between the EXO sondes and the site sonde
102 (Snazelle, 2015). This probe has been used to construct a real-time water quality monitoring
103 system with the Internet of Things (IoT) technology over estuarine and urban areas, employing a
104 combination of stationary and mobile sensors installed in multiple locations (Demetillo et al.,
105 2019; Méndez-Barroso et al., 2020; Irvine et al., 2022).

106 A bathymetric sensor, Acoustic Doppler Current Profiler (ADCP), has implemented for
107 measurement of water quantity and speed along streams and over lakes and oceans. The ADCP
108 measures the water depth and absolute current speed along the water column up to one-kilometer
109 depth at the hyper spatial resolution (vertical: up to 0.2 meters; Fong et al., 2006; Brown et al.,
110 2011; Li et al., 2018). The ADCP transmits "pings" of sound at a constant frequency into the
111 water. A high frequency pings of the ADCP yields more precise data, but it runs out of batteries
112 rapidly, and accuracy degradation of the ADPC is caused by attenuation of the signal noise ratio
113 between water and transducer due to air entrainment (Fujii et al., 2022). Water quality sensors
114 have been mounted on a boat to map horizontal variation of water quality (Gruberts et al., 2012;
115 Crawford et al., 2015). Potential opportunities of high-resolution mapping through a remotely
116 operated vehicle of water quality along rivers were explored in early 2010s (Casper et al., 2012).
117 Recently, uncrewed underwater and surface vehicles have been used for water quality mapping,
118 particularly for mixing processes of water (Amran et al., 2020; Honek et al., 2020; Griffiths et
119 al., 2022). Surveys of these vehicles are cost efficient to maintain and measure water quality and
120 quantity regularly (e.g., sub-weekly and weekly intervals). These uncrewed vehicles with water
121 quality sensors and ADCP offer a new opportunity to understand interactions of water quality
122 and quantity in aquatic environments. However, applications of these cutting-edge technologies
123 to dual monitoring of water quality and quantity along river streams and in reservoirs remains
124 limited.

125 Recently, the government of South Korea government enacted the Framework Act on
126 Water Management (FAWM). The FAWM aimed to develop the national dual monitoring
127 system of water quantity and quality. The FAWM system can monitor water quantity and quality
128 along river streams or at lakes and reservoirs at the consistent sampling time and frequency.
129 Despite such administrative efforts, the application of dual monitoring techniques for water
130 quantity and quality along rivers and in reservoirs remains lacking and this study is an attempt to
131 fill this gap.

132 This study uses an uncrewed surface vehicle (USV) with water quality sensor and depth
133 finder to conduct 30 surveys over a year for dual monitoring of water quality and quantity of a
134 small reservoir named Daljeon near the Southeastern coastline of South Korea. This study aims
135 to investigate the importance of the high-resolution mapping of water quality and depth on
136 changes in nitrate load estimates stored in the study reservoir. The USV-based dual monitoring
137 system used in this study is described in the next section. This study attempts to answer the
138 following research questions: 1) To what extent can high-resolution mapping of water quantity
139 and quality improve nutrient load estimates in the Daljeon reservoir? 2) When are the
140 uncertainties in nitrate load estimates large or small over time? 3) What are the key sources of
141 uncertainties in nitrate load estimates? This study was carried out locally; however, the findings
142 of this study will provide an insight of potential opportunities and challenges for application of
143 the current cutting-edge technologies to dual monitoring water quality and quantity, illuminating
144 the potential value of USV-based surveys for the next-generation water resources monitoring
145 system.

146 **2. Study site and data**

147 The Daljeon reservoir is used for irrigation in Pohang, South Korea (36.029 °N, 129.293
148 °E; Figure 1a). This reservoir was built in 1968 to supply water resources only for agriculture
149 during the crop planting and growing seasons (April–August) and has been managed by the
150 Korea Rural Community Corporation (KRCC). The flood water level, average water level, and
151 dead storage level of this reservoir are 47, 44 and 36 elevation meters above sea level,
152 respectively. That is, the maximum and average water depth of the reservoir is 11 and 8 meters.
153 The maximum water storage volume is 698,300 m³ (<https://rawris.ekr.or.kr/>). The maximum
154 water surface area of the study reservoir is 0.15 km², which is in Level 2 (> 0.1 km²) of the
155 Global Lakes and Wetlands Database (GLWD-2; <https://www.worldwildlife.org/pages/global-lakes-and-wetlands-database>). According to the KRCC website, the upstream land use sources
156 include 54% paddy fields, 18% forest, and 30% residential (households). In this study, 30 USV-
157 based surveys for water depth and nitrate concentration have been conducted in the Daljeon
158 reservoir for accessibility to various launching points.

159 To examine air-water interactions over the reservoir and how environmental factors may
160 affect water quality and quantity, daily precipitation and temperature data (July 2021– August
161 2022) over Pohang, South Korea are compared with our dual monitoring data for water quality
162 and quantity. The meteorological data are publicly accessible from the Korea Meteorological
163 Administration (KMA) stations (<https://www.kma.go.kr/>). In addition, the KRCC provided daily
164 measured water levels of the reservoir. We aggregated monthly nitrate concentrations of 19
165 reservoirs and 4 lakes within 100 km from the Daljeon reservoir that were retrieved from the
166 Water Environment Information System (<https://water.nier.go.kr/>). These data were used as a
167 reference for our USV measurements because of their similar land use types (e.g. paddy and
168 forest).
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170

171 **3. Materials and Methods**

172 **3.1. USV equipped with water quantity and water quality sensors**

173 In this study, SonTek's rQPOD remote control surveying package was used to mobilize
174 the water depth and water quality sensors (Figure 1). The rQPOD modular remote surveying
175 package is an uncrewed surface vehicle (USV), consisting of rQPOD and a floating platform
176 (Figure 1b). The rQPOD is installed on a floating platform and transforms it into a motorized
177 vehicle for remote operation. The rQPOD is controlled by a transmitter, Futaba T6K, at a
178 frequency of 2.4 GHz, range 500 meters (Figure 1f). The USV is equipped with a pair of trolling
179 motors, which are located on the bottom edge of both sides (Figure 1c). Our YSI EXO2 was
180 fixed at 10 centimeters depth, and ADCP was fixed at the water surface. The maximum speed of
181 the trolling motors is 1.5 m/s and the minimum depth required for the USV to collect accurate
182 data is approximately one meter. The weight of the floating platform is 4.7 kilograms. The
183 maximum payload capacity of the rQPOD is 28 kilograms. Two DJI Phantom 3 LiPO batteries
184 are used for the rQPOD operation. In this study, a floating platform with rQPOD, batteries, GPS
185 system, telemetry system, ADCP and water quality sensors are approximately 25 kilograms.
186 Detailed specifications of the rQPOD remote control surveying package is found from the
187 SonTek's website (<https://www.ysi.com/rqpod>).

188 For bathymetric measurement (water depth and velocity), the SonTek HydroSurveyor-
189 M9 Acoustic Doppler Current Profiler (ADCP), the Power/Communication Module (PCM), and
190 the SonTek Real Time Kinematic positioning GPS (RTK GPS) were mounted on the floating
191 platform. The 0.5 MHz vertical beam has an eight-degree beam angle, which can measure from
192 0.2 up to 80 m below the water surface (Figure 1e). The 1 MHz and 3 MHz doppler beams
193 (bottom tracking method) are operated with a beam angle of three-degree, which can measure
194 from 0.2 up to 40 meters below the water surface. The ADCP depth accuracy is $2 \text{ cm} \pm 1\%$ of the
195 measured depth with the highest resolution of 2 centimeters. RTK GPS provides the geo-
196 positioning data (longitude, latitude, and altitude) of the USV with a horizontal accuracy of less
197 than 0.03 m (Figure 1g). PCM supports power for ADCP and RTK GPS, using 16 units of
198 double-A batteries. It can transmit the measured data from ADCP and RTK GPS to the home
199 station laptop using telemetry operated at a frequency of 2.4 GHz. The range of the PCM
200 telemetry system is up to 500 meters. During the site surveys, the telemetry system for data
201 transmission was 200-300 meters

202 In addition, the YSI EXO2 multi-parameter sonde (EXO2) was mounted on the USV to
203 measure multiple water quality variables every second (Figure 1d). The EXO2 was installed with
204 sensors for *in situ* monitoring such as water temperature (T), pH, electro conductivity (EC),
205 dissolved oxygen (DO), and nitrate (NO_3^-) concentration. The YSI EXO nitrate smart sensor
206 ranges from 0 to 200 mg/L, and the precision is $\pm 10\%$ of reading or 2 mg/L. The sensor is able
207 to detect 63% of the change in the nitrate concentration level within less than 30 seconds
208 (Response time: $T_{63} < 30 \text{ sec}$; <https://www.ysi.com/product/id-599709/exo-nitrate-smart-sensor>).
209 The monitoring data can be logged internally on the YSI handle for on-site monitoring. The
210 nitrate concentration is measured using ion selective electrodes (ISE). Silver/silver chloride
211 (Ag/AgCl) wire electrodes are used in the nitrate ISE sensor, which is filled with a filling
212 solution. A polymer membrane separates the filling solution from the sample medium, and this
213 membrane interacts with nitrate ions. The ratio of nitrate in the sample to the internal filling

214 solution affects the electrical potential created across the membrane when the nitrate sensor is
215 placed in water. This potential difference is then measured using a pH reference electrode.
216 (Capelo et al., 2007)

217 **3.2. Sampling Survey Schedules**

218 Thirty sampling surveys were conducted in the Daljoen reservoir from July 2021
219 through August 2022 (Figure 2). Survey paths were determined by the meteorological conditions
220 of the sampling date and spatial coverage was prioritized, and we allowed for inconsistent
221 sampling paths because of limitations of the battery power of the trolling motors. The USV used
222 in this study is recommended to navigate when the wind speed is less than 8 m/s. The limitations
223 of our USV are addressed in more detail in the discussion section. These sampling survey dates
224 and IDs are shown in Table 1. We conducted the surveys between 12:00 and 15:00 on each
225 survey date to minimize potential variations of environmental conditions. The USV was
226 launched from a location in the southwest part of the reservoir. However, vegetation near this
227 launching point often blocked the view and the connectivity between the boat and remote
228 controller. After October, 1, 2021 (ID 6–30), the USV was launched at the docking spot of the
229 eastern part of the reservoir, which allowed us to survey the water quantity and quality over a
230 broader region than before. While the official battery duration of rQPOD was four to six hours
231 without instruments (nine kilograms), our USV's battery lifetime was 20–30 minutes because the
232 weight of our USV was almost three times higher than the floating platform with rQPOD. The
233 official battery duration of rQPOD was four to six hours without instruments (nine kilograms).
234 The weight of our USV was almost three times higher than the floating platform with rQPOD.
235 The USV's battery lifetime was 20–30 minutes during the early survey dates (ID1-10) when the
236 two units of the batteries were used. Since November 5, 2021 (ID 11), the power system was
237 changed with the six units of the batteries of the rQPOD to conduct a one hour-long sampling
238 survey. The remaining 20 % of the northern and western parts of the reservoir were not surveyed
239 because they were shallow (less than one meter). While the official specification of the PCM
240 connection range is 200–300 meters, the connection range of our USV varied, depending on the
241 meteorological conditions.

242 In the winter of 2021/22 (January 14 and February 11, 2022), the northern and southern
243 parts of the surface in the Daljeon reservoir were frozen. The USV surveyed water depth and
244 quality only over the middle part of the reservoir (ID 16 & 17 in Figure 2). Specific sampling
245 survey schedules and corresponding sampling ID numbers (ID 1–30) were shown in Table 1.

246 **3.3. Sensor Calibration**

247 Data logged internally on the YSI handle. According to the EXO2 manual, two-point
248 calibration (1 mg/L and 100 mg/L) was recommended for nitrate concentration calibration.
249 However, this range was too wide to apply in freshwater. In this study, four-point calibration (1,
250 2, 3, and 4 mg/L) were used. Four-level standard solutions were measured using the YSI EXO2
251 nitrate sensor over 60 minutes (Figure 3a). The corresponding potentials of 1 mg/L, 2 mg/L, 3
252 mg/L, and 4 mg/L were 141.0 ± 1.8 mV, 123.7 ± 1.4 mV, 113.0 ± 1.1 mV, and 104.5 ± 0.9 mV,
253 respectively (Fig 3). The potential difference was unstable over 10 minutes after starting
254 measurement. Low variance was observed after 10 minutes (reaching stable conditions). It is
255 worth noting that potential differences before and after stabilization were not large enough
256 (approximately 3-5%) to cross the standard solutions. Using the four-point calibration, three
257 empirical models were applied to find the best-fit model for the relationship of potential

258 difference and nitrate concentration: linear, logarithm, and exponential (Figure 3c). Based on the
 259 R-squared values (Table 2), the exponential model was selected to convert potential difference
 260 [mV] to nitrate concentration [mg/L].

261 Electrochemical sensor measurements are recommended to validate against discrete
 262 analytical chemical samples because ion chromatography of standard solutions does not account
 263 for the in-situ inferences that are always possible. Cross-validation with discrete analytical
 264 chemical samples makes electrochemical sensor measurements reliable, at least in the initial
 265 stages of qualifying an autonomous/unscrewed surface vehicles-electrochemical sensor
 266 measurement. Discrete analytical chemical samples were not collected during the study period.
 267 Instead, the USV-based nitrate concentration measurements were compared with nitrate
 268 concentrations from discrete analytical chemical samples near our reservoir, which confirmed
 269 that the YSI sensor-based measurements within the nitrate concentration ranges observed in
 270 neighboring reservoirs (Figure 7d). Traditional discrete analytical chemical samples at the study
 271 site provide a more reliable reference for further studies.

272 For electrochemical sensor equilibration and ADCP compass calibration, we used
 273 measured nitrate concentration and water depth data 10 minutes after launching the USV during
 274 each sampling survey. An ADCP compass calibration was performed over the first 10 minutes of
 275 each sampling survey to have an accurate track reference. Prior to all ADCP measurements,
 276 calibrating the internal magnetic compass of instruments with an external compass is mandatory
 277 when using GPS as the navigation reference, to ensure alignment with external compass readings
 278 (Mueller and Wagner., 2009). ADCP compass calibrations aim to calibrate out erroneous
 279 compass headings caused by sources near the ADCP and the local area.

280 3.4. Nutrient load calculations

281 The one-second water depth and nitrate data from the USV were used to create 10-meter
 282 resolution maps. To quantify the uncertainty of our sampling data from spatial variations, the
 283 coefficient of variance (CV) of the nitrate concentration data from each survey is calculated
 284 (White et al., 2008). The CV is calculated as the standard deviation divided by the mean of
 285 nitrate concentration during each sampling survey. To create the 10-meter filled map, the kriging
 286 interpolation method was used to interpolate the measured water depths and nitrate
 287 concentrations via the R software “gstat” package (Pebesma and Wesseling, 1998; Gräler et al.,
 288 2016). For variogram fitting, we utilized the ‘autofitVariogram’ function from the ‘automap’
 289 package in R, which selected the Matern model with M. Stein's parameterization (Hiemstra et al.,
 290 2009). The typical distance between two points is approximately 1.1 meters since the sampling
 291 frequency is one second and the average USV speed is 1.1 meters per second. It is worth noting
 292 that the distance between two measurement points vary slightly from run to run due to various
 293 USV speeds during the survey due to meteorological and water surface conditions.

294 We tested the sensitivity of volume estimation to spatial variations of water depth and
 295 water quality. First, we compared volume estimates using interpolated depths (iD, Eqn. 1) and
 296 the mean of depths (aD, Eqn. 2).

$$iD = w \times \sum_{i=1}^N A_i \times d_i \text{ (Eqn. 1)}$$

297 , where w is a weighting parameter for considering unmeasured surface of reservoir ($w =$
 298 $\frac{A_{\max}(t)}{\sum_i^n A_i}$, $A_{\max}(t) = A_{\max} * \frac{Wl_{\max}(t)}{Wl_{\max}}$), where A_{\max} is actual maximum area of Daljeon reservoir

299 (151,000 m²), Wl_{\max} is the maximum water level of the study reservoir and $Wl_{\max}(t)$ is the
 300 maximum water level during the sample date.), A_i is the area of the i -th grid (constant (100
 301 squared meters))), n is the number of the 10-meter by 10-meter grids we measured ($n=1, \dots, N$).

$$aD = w \times \bar{d} \times \sum_{i=1}^N A_i \text{ (Eqn. 2)}$$

302 We also calculated nitrate loads using four different equations. The first equation uses
 303 interpolated water depth and interpolated nitrate concentration of a reservoir (iDN, Eqn. 3).

$$iDN = w \times \sum_{i=1}^N (NO_3)_i \times A_i \times d_i \text{ (Eqn. 3)}$$

304 , where $(NO_3)_i$ and d_i were nitrate concentration, and water depth at the i^{th} grid, respectively.

305 The second, third, and fourth equations uses spatial averages of water depths and nitrate
 306 concentrations (aDN, Eqn. 4), the interpolated water depths and the spatial averages of nitrate
 307 concentrations (iDaN, Eqn. 5), and the spatial averages of water depths and interpolated nitrate
 308 concentrations (aDiN, Eqn. 6), respectively.

$$aDN = \bar{d} \times \overline{NO_3} \times \sum_{i=1}^N A_i \text{ (Eqn. 4)}$$

$$iDaN = w \times \overline{NO_3} \times \sum_{i=1}^N A_i \times d_i \text{ (Eqn. 5)}$$

$$aDiN = w \times \bar{d} \times \sum_{i=1}^N (NO_3)_i \times A_i \text{ (Eqn. 6)}$$

309

$$\Delta D = \frac{aD - iD}{iD} \times 100 \text{ (Eqn. 7)}$$

$$\Delta DN_j = \frac{dDN_j}{iDN} \times 100 \text{ (Eqn. 8)}$$

310 ,where j depicts the index of the difference of other nitrate load calculation methods from the
 311 "iDN" method (aDN, iDaN, aDiN–iDN for $j=1, 2, \text{ and } 3$, respectively).

312

313 3.5. Comparison spatial resolutions

314 In this study, a 10-meter spatial resolution was initially selected. The manufacturer
 315 recommended USV speed is 1.5 m/s, and the response time of YSI nitrate smart sensor (T63) is
 316 less than 30 seconds. Taking these specifications in accounts, 30- and 50-meter resolutions were
 317 chosen because the average of the USV speed was around 1.11 m/s, ranging from 0.52 m/s (ID
 318 5) to 1.62 m/s (ID 16). Given the range of USV's speed, a 30-meter resolution is suitable for the
 319 most consistent sampling surveys (1.11m/s \times 30 seconds). For the sensitivity test, we compared
 320 nitrate concentration maps at 10, 30, and 50-meter resolutions.

321 4. Results

322 4.1. Spatial variation of water depth and nitrate concentration

323 The CV of nitrate concentration was calculated over the sampling survey dates (Figure
324 4). The values of CV ranged between 0.02 (ID 30) and 0.18 (ID 11). The mean of CV values in
325 entire period were calculated 0.09 ± 0.04 (mean \pm standard deviation). In ID 18 and 30, CV
326 values were less than other surveys (CV of ID 18: 0.03, CV of ID 30: 0.02). During these
327 sampling survey dates, the survey time was short (ID 18: 13 minutes, ID 30: 22 minutes) than
328 other sampling survey dates (the sampling survey time average: 47.95 minutes). CVs were
329 higher in the first part of the sampling period (prior to January 2022). Furthermore, the
330 correlation analysis is conducted to examine the relationship between the CV of nitrate
331 concentration and other environmental and survey parameters, such as water temperature, one-
332 week accumulated precipitation, sampling time, travel distance (not shown). The variable with a
333 marginal correlation is water temperature ($r = -0.31$, $p = 0.08$). This result indicates that the CV
334 of nitrate concentration is independent with environmental and sampling parameters.

335 Spatial variations of water depths of the reservoir resembled the bathymetry of the
336 bottom of the reservoir (Figure 5). The northern and western part of this reservoir were shallower
337 than the middle part of the reservoir. The edges of reservoir were too shallow for the USV to
338 survey the water depth and nitrate concentration. In addition, aquatic plants and debris in the
339 edges made USV difficult to navigate. Moreover, vegetation and debris in the edges of the
340 reservoir made USV difficult to navigate. The spatial variance of nitrate concentrations was
341 relatively weak compared with those of water depths (Figure 6). It is worth noting that the
342 vertical gradient of temperature and nitrate concentration was not measured since this study
343 aimed to investigate the impact of horizontal resolution of the mapping of water quality and
344 quantity. These results indicate temporal changes of spatial variance of nitrate concentrations
345 across the seasons (Figure 6).

346 4.2. Seasonal variations of water temperature, water depth, and nitrate concentration

347 Pohang has strong seasonal variability of precipitation and temperature (Figure 7).
348 During the study period (July 2021–August 2022), the total precipitation was 1,430.2
349 millimeters. While the accumulated precipitation was 650.4 millimeters (47%) in July and
350 August of 2021, the total precipitation was 202.1 millimeters from June through August, 2022.

351 The mean water depth ranged between 3.4 meters (ID 29) and 7.8 meters (ID 3) (Figure
352 7c). The surveys in the late August and September, 2021 (ID 3-5) covered a larger area in the
353 southern part of the reservoir compared to the surveys in July and early August (ID 1 and 2). The
354 water levels of the Daljeon reservoir were well matched with our measured maximum water
355 depth, particularly during the sampling surveys on August 27, 2021 (ID 3) and January 14, 2022
356 (ID 15). From ID 1 to ID 3, the mean of water depth increased because of antecedent rainfall
357 events. After the summer of 2021 (ID 3), the mean water depth declined monotonically until the
358 winter of 2021/22 (ID 22), following the decreased patterns of precipitation and air temperature.
359 After ID 22 (May 2022), the water depth decreased gradually, possibly to meet an increasing
360 water demand for agriculture due to lack of rainfall in the spring of 2022.

361 4.3 Sensitivity test of water volume estimation and nitrate storage estimation

362 The water volume estimates in the reservoir followed the patterns of water depths
363 (Figure 8 (a)). The mean and standard deviations of water volumes from the iD method were

364 696,037 and 200,614 m³, respectively. The estimated water volumes from the iD method ranged
 365 between 249,788 m³ (ID 30) and 1,017,161 m³ (ID 8). The mean and standard deviations of
 366 water volumes from the aD method were 656,958 and 189,394 m³, respectively, with a range
 367 between 255,144 m³ (ID 29) and 1,004,085 m³ (ID 3). The difference between estimated water
 368 volumes of iD and aD (ΔD) ranged between -17 % (ID 9) and +2 % (ID 30), confirming that the
 369 impact of using the spatially varying data on the water volume estimate of the reservoir. We also
 370 found that the one-site measurement of water depth can underestimate the water volume of the
 371 reservoir (Figure 8b).

372 Before the survey on October 29, 2021 (ID 10), the differences of estimated water
 373 volumes from the ΔD ranged from -17.07 % and -0.13 % with the average difference, -8.10 %.
 374 After the survey ID 10, the differences of estimated water volumes from the ΔD method ranged
 375 -7.66 % to +2.65 % with the averaged difference, -3.95 %. For example, the mean of sampling
 376 time is 1,465 and 2,981 seconds before and after the ID 10 survey, respectively. The average
 377 estimated areas are 32,000 and 49,500 m², respectively before and after the ID 10 survey (the
 378 surveyed grid numbers are 11 and 20).

379 The estimated nitrate loads in the water reservoir had similar pattern with estimated
 380 water volumes (Figure 8c). The estimated nitrate loads from the iDN method ranged from 0.32
 381 (ID 30) to 3.83 tons (ID 19) with the average 2.09 ± 1.01 tons (mean \pm standard deviation, n =
 382 30, ton is metric ton). The estimated nutrients from the aDiN method ranged from 0.31 (ID 30) to
 383 3.57 (ID 19) tons with the average, 1.97 ± 0.96 ton (n = 30). The estimated nitrate loads from the
 384 iDaN method ranged between 0.32 (ID 30) and 3.84 tons (ID 19) with the average, 2.09 ± 1.02
 385 tons (n = 30). The estimated water volumes from the aDN method ranged between 0.31 (ID 29)
 386 and 3.58 tons (ID 19) with the average, 1.98 ± 0.97 tons (n = 30).

387 The difference between estimated nitrate loads of iDN and iDaN (ΔDN_2) ranged from
 388 -6.51 % (ID 1) to +2.65 % (ID 15) with and the average difference, -0.23 % (Figure 8d). The
 389 ΔDN_3 ranged from -16.80 (ID 9) % to +2.79 (ID 30) % with the average difference of -5.93 %.
 390 The ΔDN_1 was calculated in the range of -17.11 (ID 5) % to 3.23 (ID 30) %, and the mean of
 391 ΔDN_1 was -5.64 %. The difference between ΔDN_2 was smaller than other differences.

392 5. Discussion

393 5.1 Drivers of nitrate variation

394 This study found a temporal regime shift in the spatial variance of nitrate concentrations
 395 between December and January (Figure 6). After January, 2022 (ID 16), CVs in the nitrate
 396 concentration estimates declined, and the nitrate concentration estimates showed a low spatial
 397 variance over the rest of the sampling survey dates. In November and December of 2021 (ID 10
 398 to ID 15), the CVs increased. In this study, the vertical gradient of nitrate concentrations was not
 399 measured, which might induce uncertainties in nitrate load estimation. However, the proposed
 400 near surface concentration-based nitrate load calculation in this study were likely a conservative
 401 estimate (a lower boundary estimate) because it was previously found that the deep-water nitrate
 402 concentration in a reservoir is higher than surface water nitrate concentration (Paerl et al., 1975;
 403 Andersen, 1982). Thus, changes in the vertical distribution of nitrate, with depth playing a
 404 significant role, could be a factor influencing the observed CV dynamics.

405 The USV-based sampling data showed temporal changes of spatial variance of nitrate
 406 concentrations across the seasons. After heavy rainfall (ID 3), the nitrate concentration increased
 407 dramatically (from 1.07 to 3.53 mg/L). The result indicates potential non-point nutrient inflows

408 from surrounding areas after heavy rainfall events (Uttormark et al., 1974; Zhao et al., 2022).
409 The highest recorded precipitation rate during these storms was 43.1 mm/hour on August 24,
410 2021. In the summer of 2022, however precipitation was not intense to increase nitrate
411 concentration in the reservoir through non-point nutrient inflows. Assessment of the threshold
412 precipitation value for triggering non-point nitrate inflows still remains limited, which can
413 provide an actionable information for an effective water and land management, particularly the
414 control of nutrient inflows.

415 The nitrate concentration estimates a high-to-low seasonal regime shift between
416 December and January because horizontal and vertical mixing of lake and reservoir were
417 accelerated by wind speed and air temperature in the winter and spring (Woolway et al., 2020).
418 From sampling surveys during the spring months (ID 17 through ID 19; February to March
419 2022), the nitrate concentration was high, which is in line with the finding of other sites
420 (Domogalla et al., 1926; Seike et al., 1990). After ID 19, the nitrate concentration began to
421 decrease. Potential causes of the decreased nitrate concentrations are a denitrification and
422 biological removal of nitrate concentration during the spring and summer months. In the Daljeon
423 reservoir, algal blooms were observed visually in summer 2021 and spring 2022, and nutrient
424 concentration were related with algal biomass (Smith, 1982; Paerl et al., 2001). It is known that
425 the biological removal rate of nitrate concentration is also affected by water temperature
426 (Hamilton and Scdhladow, 1997). Another possible cause is the sinking of nutrient to the bottom
427 sediment (Chapra, 1982). In July and August of 2021, intense rainfall events visually increased
428 the turbidity from suspended sediment and increased nitrate concentration by measurement.
429 However, in the summer of 2022, precipitation was not enough to increase nitrate concentration
430 in the reservoir (average daily precipitation in summer 2021: 10.84 mm/day, in summer 2022:
431 2.25 mm/day). These results confirmed the importance of precipitation intensity on non-point
432 nitrate transports.

433 This study found that the disparity in $\Delta DN2$ was notably less pronounced than other
434 variations. It implied that more accurate water volumes at the high spatial resolution play a
435 dominant role in nitrate storage estimation than high-resolution nitrate concentration
436 measurement. However, the resolution of nitrate concentration sampling is significant,
437 depending on the season and the characteristic of a reservoir and surrounding environments. The
438 Daljeon reservoir is relatively small and has the spatially homogeneous spatial distribution of
439 nitrate concentration (Figure 6), resulting in a dominant role of water depth in nitrate load
440 estimation.

441 **5.2 Limitations of the USV approach**

442 Our USV has encountered several fundamental limitations. The first limitation is the
443 limited spatial coverage due to the battery lifespan (< 1.5 hours) and floating debris. Given the
444 average navigation speed (1.1 m/s), the USV can travel over the lake up to around six kilometers
445 of the survey path. Intense rainfalls bring a significant amount of floating debris into the lake,
446 which is various, depending on the season and precipitation intensity (Anderson and Sitar, 1995;
447 Yuan et al., 2005). For example, the ID 29 and 30 surveys measured the water quality and depth
448 over relatively small areas of the lake mainly due to floating debris from antecedent significant
449 precipitation and runoff. We faced challenges in collecting accurate data from ID 1 to ID 10,
450 resulting in low confidence in our interpolations. This limitation arose because the battery life of
451 our USV was shorter than specified by the manufacturer. To overcome this issue, we added four
452 additional batteries for sampling after ID 10. Instead of discarding the data prior to ID 10, we

453 chose to report it with low confidence to share our experiences and the progress made with this
454 technology. Another limitation we encountered was the inability to collect homogeneous and
455 regular data. The manufacturer of the rQPOD, our USV, provides an auto-navigation technology.
456 We attempted to utilize this feature for sampling. However, we faced challenges such as having
457 to replace batteries midway due to their short life, as well as issues with the USV's movement
458 caused by wind and debris (minor environmental problems). As a result, we relied on a remote
459 controller for data collection and made efforts to maintain a consistent and regular path for the
460 boat. Overall, we acknowledge the technical limitations we faced with our USV and have made
461 various adjustments and adaptations to address these challenges.

462 The interpolation-based spatial maps have uncertainties related to the estimation of the
463 actual water surface area of the study reservoir on the sampling date. In this study, the actual
464 water surface area on the was calculated by multiplying the ratio of the maximum water surface
465 area to the maximum water level by the maximum water level during the sampling date. The
466 proposed method might not capture a complex bathymetry of the reservoirs (see Figure 5). To
467 reduce these uncertainties, combining USV-based surveys with other new technologies, such as
468 drones and remotely operated vehicles, is required (Song et al., 2023). Recently, three
469 dimensional (3-D) lake topography modeling and deep learning techniques with UAV-captured
470 imagery data have been applied to estimate the water surface area and water volume in a
471 reservoir/pond (Fang et al., 2023; He et al., 2023). Our results showed that there were low CV
472 values and weak spatial nitrate variations over the entire study period, except for the fall,
473 indicating that the reservoir undergoes a strong mixing event once a year, suggesting a
474 monomictic lake. To understand mixing processes, the vertical measurement of nitrate
475 concentrations is required, which can be measured by autonomous underwater vehicles
476 (Merrifield et al., 2023).

477 The YSI nitrate smart sensor, while effective, has certain inherent limitations regarding
478 accuracy and response time. To address these challenges, we have developed an innovative
479 approach to sensor calibration and validation. Traditionally, using these sensors in the field has
480 been problematic when it comes to verifying measured concentrations (Aubert et al., 2014; Rode
481 et al., 2016a; Rode et al., 2016b). Previous research has attempted to validate the sensors through
482 lab experiments (Capelo et al., 2007; Bowling et al., 2016). However, this conventional approach
483 requires additional equipment and techniques to measure chemical concentrations (Beaton et al.,
484 2012). Recently, Samuelsson et al. (2023) highlighted that excessive reliance on laboratory
485 measurements can introduce uncertainties due to the nature of laboratory experiments. They
486 found that more consistent calibration can improve accuracy. In our study, we employed ion
487 chromatography to measure standard solutions, and the results aligned well with the intended
488 concentrations of nitrate standard solutions (1, 2, 3, and 4 mg/L). Subsequently, we proposed a
489 sensor calibration and validation method to measure water depths and nitrate concentrations in
490 the Daljeon reservoir. Most of the nitrate concentration measurements were close to the upper
491 bound of the nitrate concentration range among 23 neighboring lakes/reservoirs. These high
492 nitrate concentrations might be caused by multiple sources including more are of paddy in the
493 watershed, more intense farming of the paddy fields, and more accurate estimate of nitrate
494 concentration estimates from high-resolution mapping. To investigate a true cause of these high
495 nitrate concentration estimates, an inter-comparison study with measurements from neighboring
496 lake/reservoirs is necessary. Furthermore, we observed that the concentrations reported by the
497 YSI device were overestimated for standard solution concentrations of 2, 3, and 4 mg/L (Figure
498 3c). This observation suggests that the two-point sensor calibration (1 and 100 mg/L)

499 recommended by YSI was not as accurate within lower concentration ranges. Therefore, we
500 propose that our sensor calibration and validation method could be a viable approach to enhance
501 the accuracy of the YSI nitrate smart sensor and other similar ISE sensors.

502 In this study, the the response time of the YSI nitrate sensor ($T_{63} < 30\text{sec}$) was a crucial
503 factor influencing the decision of an appropriate spatial resolution of water depth and nitrate
504 maps. We conducted a sensitivity test to the horizontal spatial resolution of interpolation of water
505 depths and nitrate concentrations on November, 26 2021 (ID 13) and April 22, 2022 (ID 21)
506 when the CVs were higher and lower than the average (0.09 of CV), respectively (0.16 and 0.08
507 for ID 13 & 21, respectively). The differences of the nitrate load estimates among the 10, 30, and
508 50-meter resolution maps were clearer on the ID 13 survey compared to the ID 21 survey (Figure
509 9). For the ID 13 survey, the nitrate load estimates were 2.44, 2.51, and 2.57 tons from the 10,
510 30, and 50-meter resolution maps, respectively. The 50-meter resolution map overestimated +5%
511 of nitrate load compared to the 10-meter resolution map. On the other hand, the ID 21 survey
512 date with a low CV value showed no significant impact of the horizontal spatial resolution for
513 nitrate load mapping. These results underscore the importance of high spatial resolution mapping
514 on reducing the nitrate load estimate in a reservoir/lake.

515 **5.3 Challenges of the USV approach**

516 This study found that USV-based water volume estimates of the Daljeon reservoir was
517 $696,037 \text{ m}^3$ on average over the study period. The maximum water volume estimate was
518 $1,017,161 \text{ m}^3$ in October, 2021 (ID 8), which was larger than the design maximum capacity
519 ($698,300 \text{ m}^3$) by 57%. This discrepancy may be attributed to rehabilitation and upgrade of the
520 reservoir. The Daljeon reservoir has been rehabilitated with two maintenance projects in 2015
521 and 2022. The KRCC local authority confirmed that the 2015 and 2022 projects included the
522 construction of waterways for paddy fields and the construction of an emergency water gate,
523 respectively. Other than these two projects, the KRCC irregularly conducted dredging to manage
524 the reservoirs, but no official records were available before 2012. The findings of this study
525 implied that other reservoirs constructed in the 1960s and 1970s like the Daljeon reservoir might
526 have significant uncertainties in the designed maximum capacity, which requires a regular
527 inspection program for bathymetry survey.

528 In this study, we monitored water volume and nitrate concentration simultaneously via
529 the USV equipped water depth and quality sensors. Marcé et al. (2016) reported the importance
530 of simultaneous management of water quality variables (chemical) and ecosystem compounds
531 (biological) in lake and reservoir management. Furthermore, Pomati et al, (2016) emphasized the
532 importance of water quantity and biological compounds for lake water managements. Mounting
533 sensors for chlorophyll *a* or fluorescent dissolved organic matter concentrations on the USV will
534 provide important information of interactions between water quantity and quality and their
535 ecological impacts (Bowling et al., 2016; Liu and Georgakakos, 2021).

536 Recently, the Surface Water and Ocean Topography (SWOT) satellite was launched in
537 December 2022 (<https://swot.jpl.nasa.gov/>). Capabilities of the SWOT mission for terrestrial
538 hydrology were introduced as a global-scale monitoring system of surface water storage change
539 and fluxes at the hyper-resolution (about 50–200 meters) (Biancamaria et al., 2015). While the
540 capability of the SWOT to detect extreme U.S. flood events was reported based on SWOT's orbit
541 ephemeris (Frasson et al., 2019), the SWOT satellite data are required for site-specific validation
542 over not only U.S. but also other countries. It also has uneven temporal sampling of surface
543 water storage change, which requires a combination of in situ data from other sources. This study

544 hinted how the SWOT satellite data can be facilitated by combining the USV-based
545 measurement as a reference and complementary data source.

546 **6. Conclusions**

547 This study succeeded to conduct a one-year long surveys of dual monitoring of water
548 quality and quantity in a small-size monomictic artificial lake in South Korea at a
549 spatiotemporally consistent scale using an uncrewed surface vehicle with ADCP and a probe
550 with multiple environmental electrochemical sensors. This study demonstrated that the nutrient
551 load estimates from a one-site monitoring site can be underestimated compared to those from
552 spatially varying measurements of water quality and depths. This study found that water depth
553 appears to be more important than nitrate concentration in the load estimates. Moreover, this
554 study found that the relative importance of water depth and nitrate concentration on the nitrate
555 load estimation vary temporally when the spatial variability of nitrate concentration is strong,
556 particularly during the winter months when the wind speed is high.

557 This study examined the applicability and practicability of USV to dual monitoring of
558 water quality and quantity. The one year-long dual monitoring data of water quality and quantity
559 of the Daljeon reservoir proved that the USV with ADCP and electrochemical sensors was a
560 costly efficient tool and a step in the development of future technologies. This study also
561 discussed some limitations and challenges of the dual monitoring system via the USV, ADCP,
562 and YSI electrochemical sensors used in this study. Particularly, the USV technology used in
563 this study had the limited sampling survey time and spatial coverage. This USV employment is
564 one step in the development of future technologies. Combining the USV-based approach with
565 other techniques, such as stationary sensors and uncrewed aerial vehicles, uncertainties in
566 measuring the water surface extent can be reduced.

567 This study emphasized the importance of an initiative effort to apply cutting-edge
568 technologies on developing the next-generating water monitoring system for nitrate load and
569 further environmental implications. More reliable technologies might be available but high-
570 priced. Research and development budgets should support research opportunities to develop the
571 next-generation water monitoring system, which eventually will provide new challenges and
572 opportunities to investigate the coupled dynamics of water quantity and quality and help develop
573 a more efficient and effective water resources monitoring and management system for
574 sustainable development of our communities.

575

576 **Authorship contribution statement**

577 **Kwang-Hun Lee:** Conceptualization, Data curation, Investigation, Formal analysis,
578 Methodology, Software, Validation, Visualization, Writing – original draft, Writing – Review &
579 Editing. **Shahid Ali:** Analysis, Validation, Writing – Review & Editing. **Yena Kim:** Validation,
580 Writing – Review & Editing. **Kitack Lee:** Analysis, Validation, Writing – Review & Editing.
581 **Sae Yun Kwon:** Analysis, Validation, Writing – Review & Editing. **Jonghun Kam:**
582 Conceptualization, Methodology, Funding acquisition, Project administration, Resources,
583 Supervision, Writing – review & editing.

584 **Declaration of competing interest**

585 The authors declare that they have no known competing financial interests or personal
586 relationships that could have appeared to influence the work reported in this paper.

587

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592

593 **Data Availability**

594 The data and python codes used in the study are available at Harvard Dataverse via
595 <https://doi.org/10.7910/DVN/KBHXBN>.

596

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828

829 **List of Table Captions**

830

831 Table 1. Sampling survey schedules and corresponding sampling ID numbers (ID 1–30). An
 832 asterick depicts the first survey when the power system is changed for increase sampling time of
 833 the USV.

834

835 Table 2. Estimated parameters of three empirical models for the potential difference-nitrate
 836 concentration relation using four-level standard solutions.

837

838 **List of Figure Captions**

839

840 Figure 1. Maps of the Daljeon reservoir in Pohang in South Korea (a) and USV-based survey
 841 systems: Uncrewed surface vehicle ((b) & (c): top and bottom view, respectively), multi-
 842 parameter sonde (YSI-EXO2) (d), ADCP (e), remote controller (f), and GPS receiver (g). Red
 843 and blue circles in (a) depict the launching point of the USV before and after ID 6, respectively.

844

845 Figure 2. Maps of the paths of the 30 USV-based surveys in the Daljeon reservoir with 10m x
 846 10m grids.

847

848 Figure 3. Measured potential difference of nitrate standard solutions using the YSI nitrate sensor
 849 over time a), relationship nitrate concentration with potential difference (b). In (a), red, green,
 850 blue, and purple lines depict measured potential difference of the standard solutions at 1, 2, 3,
 851 and 4 mg/L of nitrate concentration, respectively. In (b), black solid, gray dash and gray solid
 852 lines depict exponential, linear, and logarithm functions, respectively. Measured concentration of
 853 nitrate standard solution (x-axis) and from the YSI (y-axis) (c).

854

855 Figure 4. Coefficient of variances of nitrate concentration during 30 USV-based surveys. Shaded
 856 area colored in gray depict the period of the launching point at the southwestern part of reservoir.

857

858 Figure 5. 10-meter resolution maps of water depths of the Daljeon reservoir during 30 USV-
 859 based surveys.

860

861 Figure 6. 10-meter resolution maps of nitrate concentrations of the Daljeon reservoir during 30
 862 USV-based surveys.

863

864 Figure 7. Seasonal variations of meteorological and water surface conditions: air and water
 865 temperature in Pohang region and Daljeon reservoir, respectively (a), precipitation in Pohang
 866 region (b), water depths (c) and nitrate concentration (d) in the Daljeon reservoir. In (a), red,
 867 black, and blue lines depict daily maximum, average, and minimum air temperatures,
 868 respectively, and open circles depict measured water temperature. In (c), a red line depicts the
 869 maximum water depths measured by KRCC and circle markers and error bars depicts water
 870 depth averages and standard deviations measured by USV. In (d), circle markers and error bars
 871 depict nitrate concentration averages and the minimum-maximum range measured by USV. Red
 872 box plots in (d) depict nitrate concentration of the 23 neighboring lakes.

873

874 Figure 8. Temporal variation of water volume and nitrate storage estimation by calculating
875 method (a, c, respectively); (a) circle: water volume estimation using interpolated water depth,
876 grey circle: water volume estimation using mean of water depth (iD), (b) the difference of water
877 volume using interpolated water depth between using mean of water depth (ΔD), (c) nitrate loads
878 using interpolated water depths and nitrate concentrations (iDN), and (d) the difference of nitrate
879 storage using interpolated water depth and interpolated nitrate concentration between other
880 methods (aDN, iDaN, and aDiN-iDN for $j = 1, 2,$ and $3,$ respectively). Gray box is period of
881 when we docked the boat on the SW part of reservoir.

882

883 Figure 9. Nitrate concentration maps ((a)-(f)) and nitrate load estimates ((g) and (h)) of the ID13
884 and 21 sampling survey at 10-, 30-, and 50-meter resolutions.

885

886 Table 1. Sampling survey schedules and corresponding sampling ID numbers (ID 1–30). An
 887 asterick depicts the first survey when the power system is changed for increase sampling time of
 888 the USV.

ID	Sampling date	Sampling time [min]	Travel distance [m]
1	July 23, 2021	45.93	1.95
2	July 29, 2021	20.95	1.44
3	August 27, 2021	15.30	1.08
4	September 01, 2021	17.18	1.29
5	September 10, 2021	18.02	0.57
6	October 01, 2021	15.50	1.25
7	October 08, 2021	20.80	1.46
8	October 15, 2021	17.68	1.41
9	October 22, 2021	12.50	0.94
10	October 29, 2021	16.87	1.29
11*	November 05, 2021	63.13	3.77
12	November 19, 2021	67.55	4.61
13	November 26, 2021	46.90	3.80
14	December 10, 2021	37.52	2.79
15	December 24, 2021	59.25	4.77
16	January 14, 2022	15.60	1.52
17	February 11, 2022	39.78	3.25
18	March 11, 2022	13.40	1.02
19	March 25, 2022	70.92	3.98
20	April 15, 2022	49.67	3.54
21	April 22, 2022	60.43	4.49
22	May 06, 2022	60.80	4.40
23	May 20, 2022	88.55	4.03
24	June 03, 2022	29.27	2.21
25	June 17, 2022	47.83	3.60
26	July 01, 2022	55.20	4.20
27	July 19, 2022	58.40	4.51
28	August 12, 2022	38.70	2.95
29	August 25, 2022	68.58	3.45
30	August 26, 2022	22.35	0.83

889

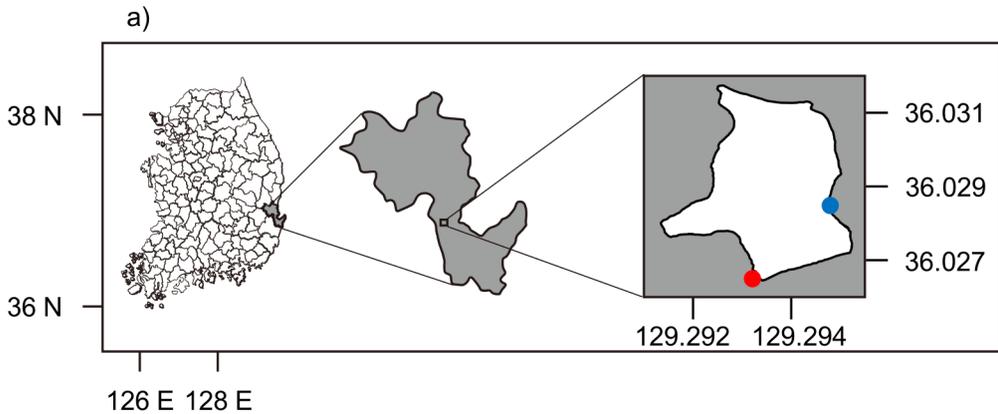
890

891 Table 2. Estimated parameters of three empirical models for the potential difference-nitrate
892 concentration relation using four-level standard solutions.

Line types	Empirical model equation	R ²
Linear	$y = -0.08 x + 12.26$	0.972
Logarithm	$y = -9.96 \ln(x) + 50.17$	0.985
Exponential	$y = 221.05 \exp(-0.038x)$	0.998

893

Figure 1.



b)



c)



d)



f)



e)



g)



Figure 2.

Figure 3.

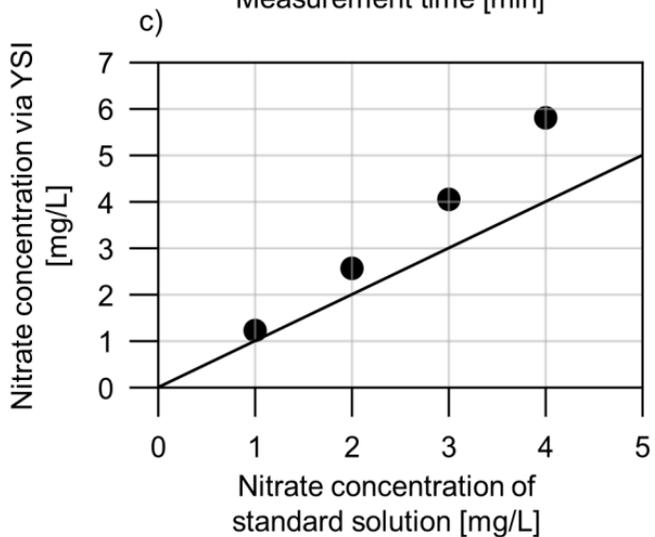
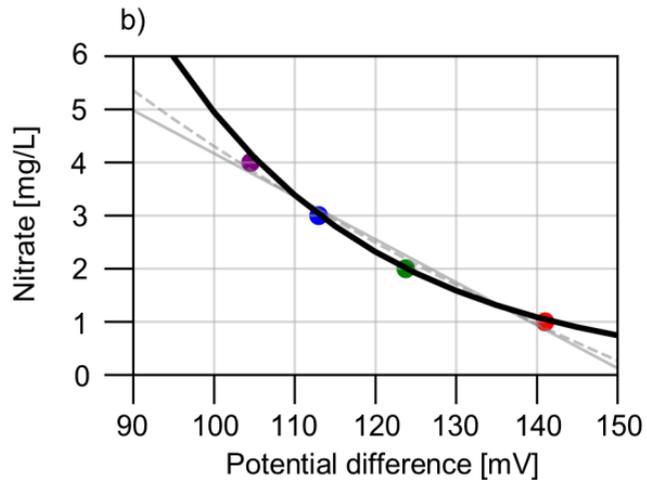
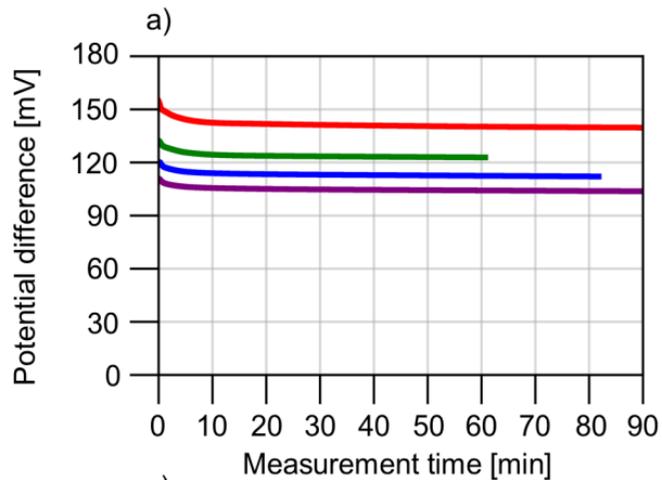


Figure 4.

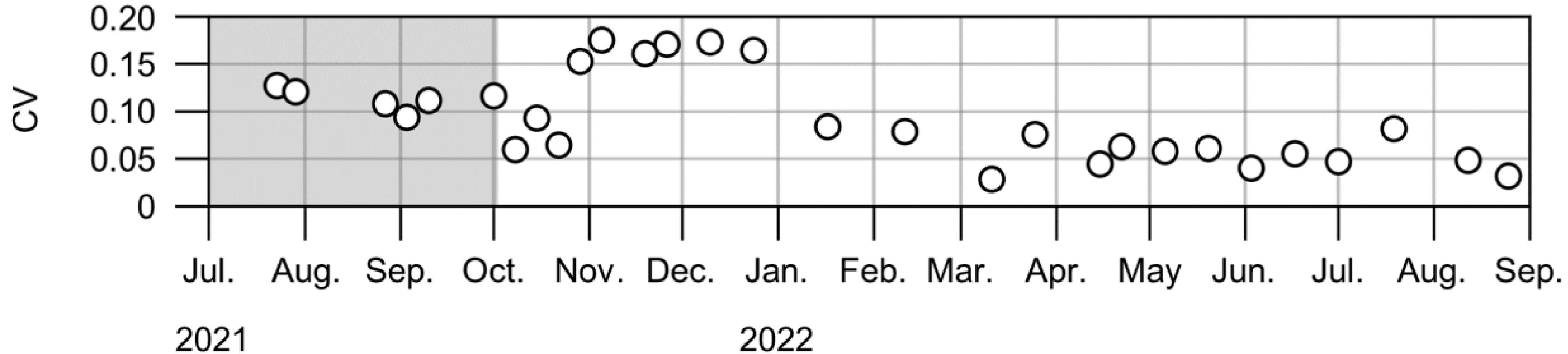


Figure 5.

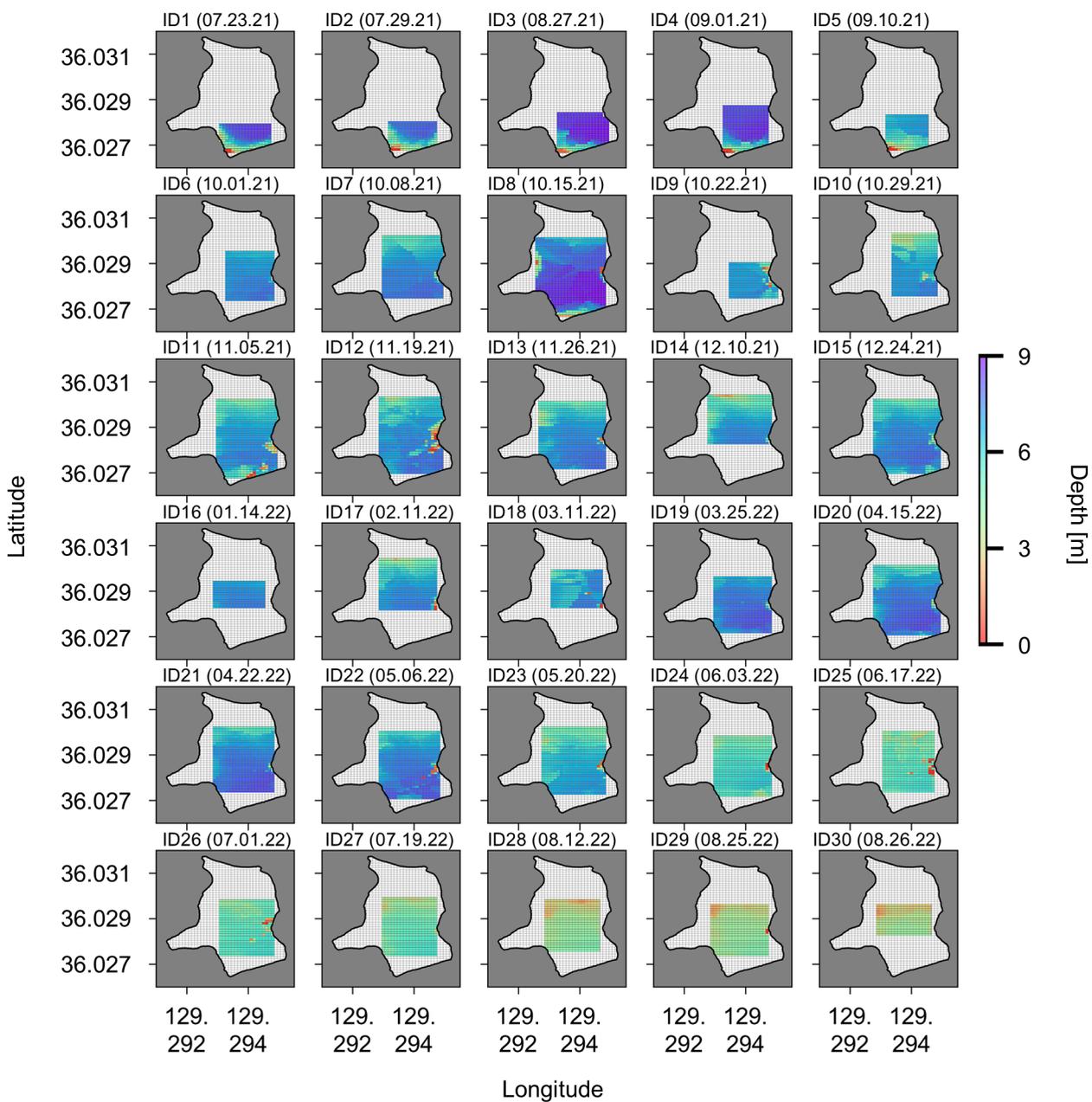


Figure 6.

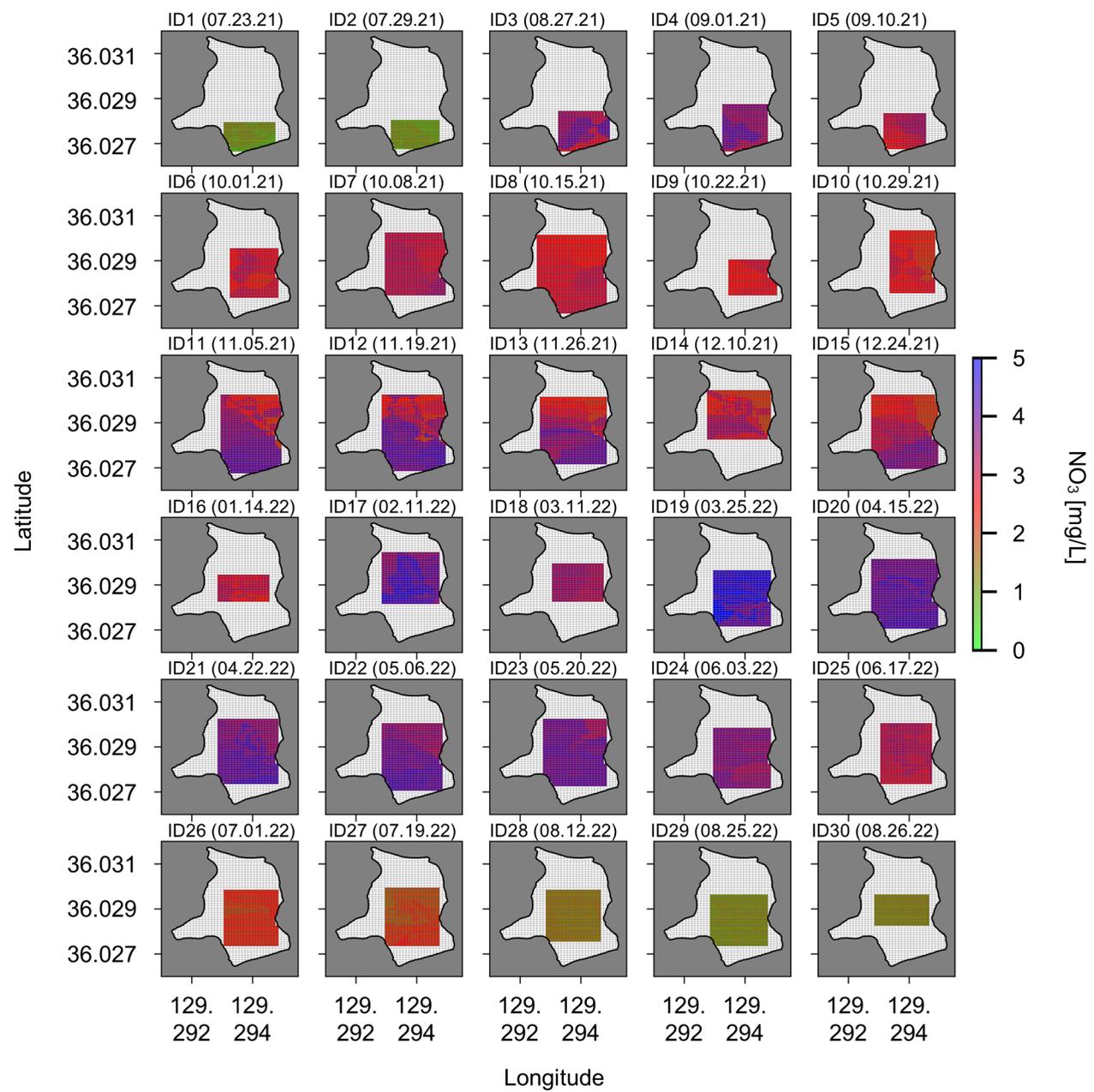


Figure 7.

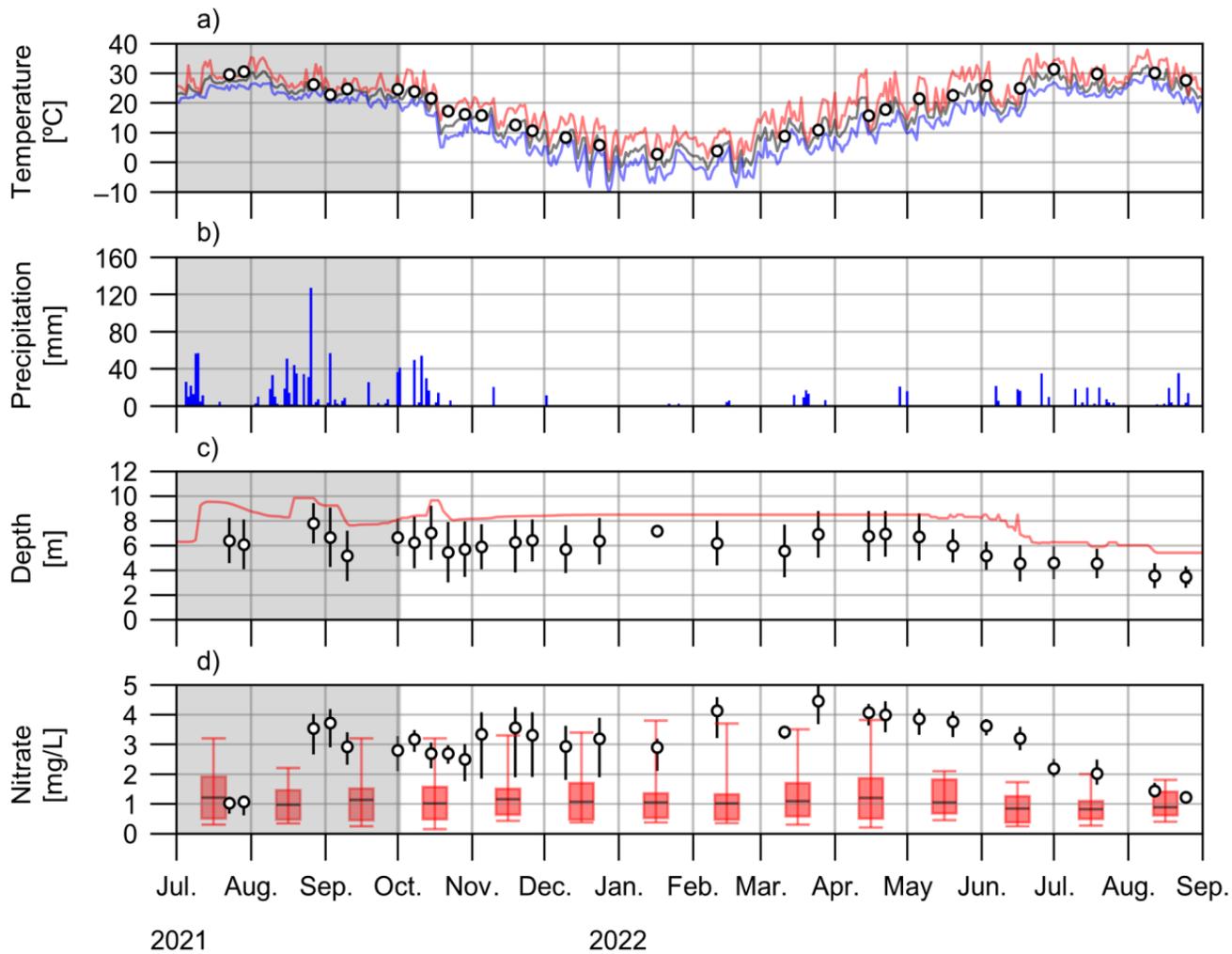


Figure 8.

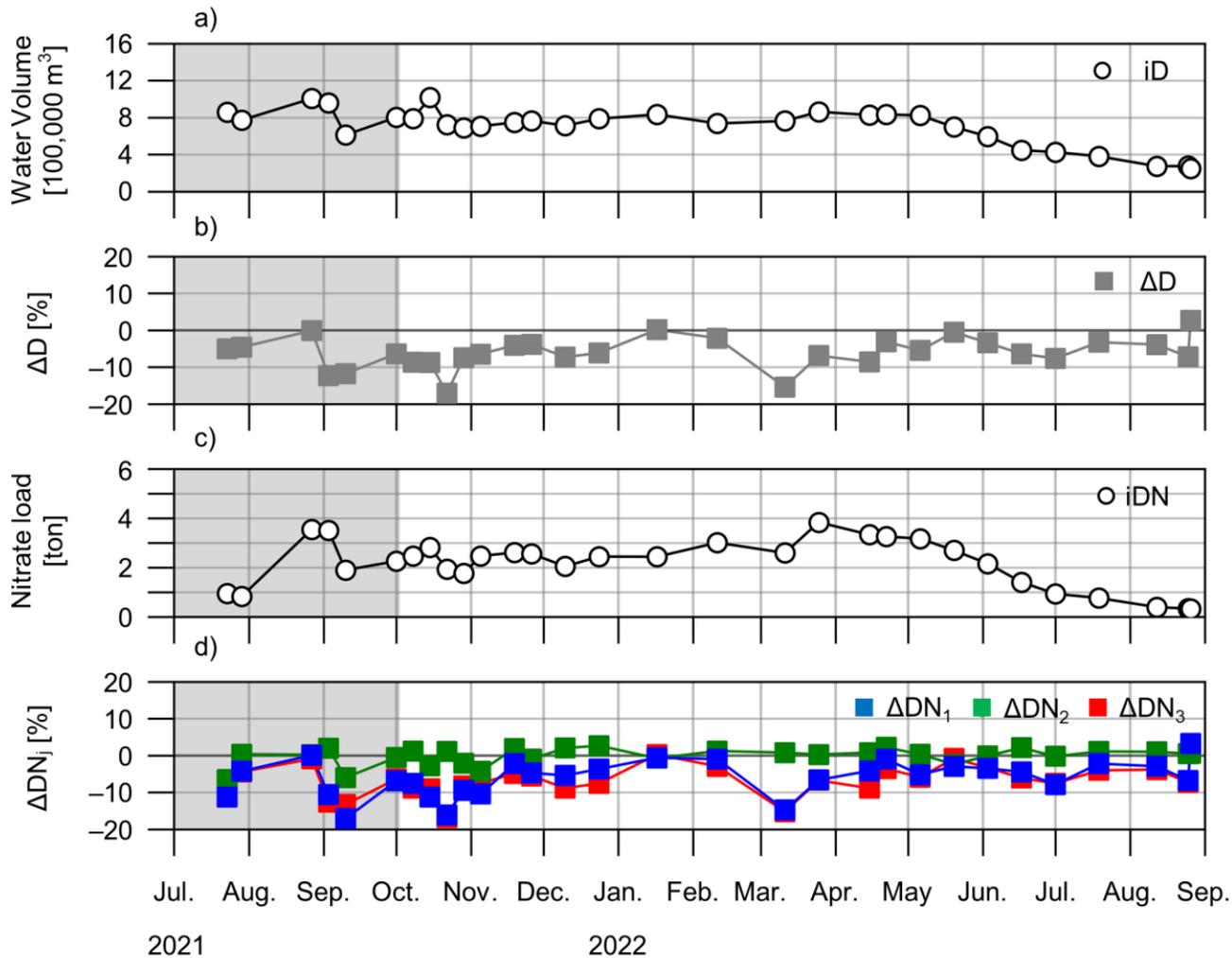


Figure 9.

