2	Giulia Valerio ¹ , Marco Pilotti ^{1,4} , Maximilian Peter Lau ^{2,3} , Michael Hupfer ²
3	¹ DICATAM, Università degli Studi di Brescia, via Branze 43, 25123 Brescia, Italy
4	² Leibniz-Institute of Freshwater Ecology and Inland Fisheries, Müggelseedamm 310, 12587 Berlin,
5	Germany
6 7	³ Université du Quebec à Montréal (UQAM), Department of Biological Sciences, , Montréal, QC H2X 3Y7, Canada
8	⁴ Civil & Environmental Engineering Department, Tufts University, Medford, MA 02155, USA
9 10 11	Correspondence to: Giulia Valerio (giulia.valerio@unibs.it)
12	Abstract

Oxycline oscillations induced by internal waves in deep Lake Iseo

13 Lake Iseo is undergoing a dramatic de-oxygenation of the hypolimnion, representing an emblematic example among the deep lakes of the pre-alpine area that are, to a different extent, undergoing 14 reduced deep-water mixing. In the anoxic deep waters, the release and accumulation of reduced 15 substances and phosphorus from the sediments are a major concern. Because the hydrodynamics of 16 17 this lake was shown to be dominated by internal waves, in this study we investigated, for the first time, the role of these oscillatory motions on the vertical fluctuations of the oxycline, currently 18 19 situated at a depth of approximately 95 m, where a permanent chemocline inhibits deep mixing via convection. Temperature and dissolved oxygen data measured at moored stations show large and 20 21 periodic oscillations of the oxycline, with an amplitude up to 20 m and periods ranging from 1 to 4 days. Deep motions characterized by larger amplitudes at lower frequencies are favoured by the 22 excitation of second vertical modes in strongly thermally stratified periods and of first vertical modes 23 in weakly thermally stratified periods, when the deep chemical gradient can support baroclinicity 24 regardless. These basin-scale internal waves cause a fluctuation in the oxygen concentration between 25 0 and 3 mg L⁻¹ in the water layer between 85 and 105 m depth, changing the redox condition at the 26 sediment surface. This forcing, involving approximately 3% of the lake's sediment area, can have 27 major implications for the biogeochemical processes at the sediment-water interface and for the 28 internal matter cycle. 29

30

31 **1. Introduction**

Physical processes occurring at the sediment-water interface of lakes crucially control the fluxes of chemical compounds across this boundary (Imboden and Wuest, 1995) with severe implications for water quality. In stratified lakes, the boundary-layer turbulence is primarily caused by wind-driven internal wave motions (Imberger, 1998). Consequently, the periodicity of these large-scale oscillations contributes to unsteadiness in the sediment–water flux (Lorke et al., 2003).

37 One reason for non-stationarity is the action of alternating velocity currents at the top of the benthic 38 boundary layer (BBL), as theoretically explained by Jørgensen and Marais (1990) and Lorke and Peeters (2006). In the immediate vicinity of the water-sediment interface, the vertical transport of 39 40 solutes occurs via molecular diffusion in the diffusive sublayer. The thickness of this layer, which is solute-specific and on the order of few millimetres, strongly depends on the flow regime in the 41 42 turbulent BBL above. Increased turbulence results in a compression of the diffusive sublayer and, according to Fick's first law, an increase in the solutes fluxes. These alternating currents are the main 43 reason for transient variations in the sediment oxygen uptake rate and penetration depth as 44 experimentally observed by Lorke et al. (2003), Brand et al. (2008) and Bryant et al. (2010) in Lake 45 46 Alpnach, a 34 m deep lake known to feature pronounced seiching.

In thermally stratified lakes, a further driver of flux unsteadiness is the periodic occurrence of cyclic 47 48 convective turbulence in the sediment area exposed to pronounced temperature oscillations of the 49 overlying water during internal seiches. During the upslope current, cold deep water flows over the warmer sediments. The resulting intermittent instability drives free convection and accelerates the 50 fluxes at the sediment-water interface by more than one order of magnitude, as experimentally 51 observed by Kirillin et al. (2009), Lorke et al. (2005) and Chowdhury et al. (2016). In lakes with 52 anoxic water layers, the seiches-induced oscillations can be accompanied by periodical changes in 53 the oxygen concentration in a large internal shoreline area as described by Deemer et al. (2015) for 54 Lacamas Lake. Bernhardt et al. (2014) observed similar seiches-induced oxygen fluctuations at the 55 sediment-water interface in the shallower area of the eutrophic Lake Arendsee resulting from the 56 57 formation of a distinct metalimnetic oxygen minimum during summer.

These findings motivated us to assess whether similar unsteady fluxes also occur in deep lakes where incomplete seasonal mixing creates a deep oxycline between the mixolimnion and a perennially stagnant and denser monimolimnion. The density gradient that is typically present across these layers has been shown to support higher vertical baroclinicity (Salvadé et al., 1988; Roget et al. 2017), whose amplitude is typically larger than that of the thermocline. Accordingly, we hypothesize that under the deep oxycline motions, the contiguous sediments undergo alternating redox conditions, with entailing implications for biogeochemical processes controlling the phosphorus (P) fluxes at the sediment–water interface. In a previous study, a three-layer model of the 288 m deep and meromictic Northern Lake Lugano predicted the oscillation of the deep chemocline to be up to 10 times greater than that of the thermocline (Salvadé et a, 1988). Hutter (2011) later invoked a field verification of these computational results. Although the oxygen gradient across deep oxyclines (e.g. in meromictic lakes) can be pronounced and typically persists beyond seasonal stratification, field investigation of the oxycline seiching remains unavailable.

71 A suitable field site for this type of investigation is Lake Iseo, a deep lake where a chemocline at approximately 95 m separates 4.7 km³ of oxygenated waters (mixolimnion) and 3.2 km³ of anoxic 72 waters (monimolimion). During the thermally stratified period, high-resolution temperature data 73 (Pilotti et al., 2013) highlighted a strong internal wave activity in the first 50 m. Here the main ~25 h 74 period mode (first vertical, first horizontal mode, or V1H1) is excited by the ordinary wind and is 75 76 occasionally superimposed on a ~60 h period mode (second vertical, first horizontal mode, or V2H1), 77 the latter being excited by long-lasting winds. The occurrence of these motions was interpreted as the 78 outcome of wind forcing with similar horizontal structures and with energies at frequencies near the 79 free oscillations of the excited modes (Valerio et al., 2012). In this study, we extended this analysis to wind-induced movements of the waters between 85 and 105 m, where the oxycline forms, to 80 provide an estimation of the spatial and temporal extent of oxygen fluctuations at the sediment 81 surface. As sediments are generally known to be potentially redox-sensitive P sinks, we discuss our 82 results in light of expected P fluxes from the contiguous sediments. The importance of this research 83 is emphasized by the observation that Lake Iseo is currently undergoing a change in mixing pattern 84 and P recycling, such that a deeper understanding of the sediment P release dynamics is crucial in 85 forecasting the possible future trajectory of this ecosystem. 86

87

88 **2.** Methods

89 **2.1 Field site**

Lake Iseo (see Fig. 1) is 256 m deep and 61 km² in area. It is located in the pre–alpine area of Italy, at the southern end of Valle Camonica, a wide and long glacial valley. In the first limnological study of Lake Iseo, completed in 1967, the lake was described as a monomictic and oligotrophic lake, featuring a fully oxygenated water column and P concentrations of a few μ g L⁻¹. Beginning during the 1980s, the accumulation of solutes from biomass deposition, in combination with climatic factors, has gradually inhibited deep water renewal, causing a persistence of anoxic conditions and an increase

in P concentration (Garibaldi et al., 1999). During April 2018 we measured the chemocline and the 96 oxycline at a depth of 95 m (see Fig. 2a). The density difference between the mixolimnion and the 97 monimolimnion, calculated at approximately 25 mg L⁻¹ (Scattolini, 2018), seems to be sufficient, 98 under current climatic conditions, to prevent deeper convective mixing. In the anoxic 99 100 monimolimnion, the P concentration (currently with a space averaged value of $\sim 111 \,\mu g \,\text{TP}\,\text{L}^{-1}$) does not show any reduction, and a recent field campaign has shown that the P stock increases by 101 approximately 30 tons of P year⁻¹ through mineralization of material received from above water layers 102 (Lau et al., in preparation). 103

104

105 2.2 Field data

A wide set of experimental data was measured at the lake stations shown in Figure 1 to describe the 106 wind-induced movements of the water layers in the mixolimnion and monimolimnion of Lake Iseo. 107 Two on-shore stations measured wind speed and direction, air temperature, air humidity, and short-108 109 wave radiation (SS-N and SS-S) at a high temporal resolution (60 s). Furthermore, a floating station (LS-N) measured wind speed and direction and net long-wave radiation. LS-N is further equipped 110 111 with eleven submerged loggers that measure the temperature ($\pm 0.01^{\circ}$ C accuracy, 60 s interval), providing data regarding the vertical movements of the thermal profile (see Fig. 2b). During October 112 113 2017, we added three additional temperature loggers at 55, 75 and 113 m depth to better describe the temperature fluctuations below the thermocline given their higher accuracy ($\pm 0.002^{\circ}$ C). 114

The LS-S logger chain was installed at 105 m depth in the southern basin. To capture the vertical 115 fluctuations in the oxycline, we installed four submersible instruments (miniDOT, Precision 116 Measurement Engineering, Vista, Ca, USA) between 85 and 105 m depth, and measured dissolved 117 oxygen (DO) for nine consecutive months at a 60 s^{-1} sampling frequency (see Table 1). These loggers 118 rely on a fluorescence-based oxygen measurement with an accuracy of \pm 5% of the measured value 119 (mg L⁻¹). Two miniDOT loggers were also installed at the northern station (LS-N) at 85 and 95 m. 120 depth. As shown in Table 1, NO85 and NO95 measured the oxygen concentration at the same depths 121 122 as those of the southern instruments, but operated for a shorter period of time. In the following sections, we will focus on describing the data analysis from July 2017 to February 2018 that fully 123 captures the oxygen concentration evolution during the transition from a strongly to a weakly 124 stratified period. 125

On the 21th and 22nd of July 2017, we also conducted a field campaign aimed at investigating the oxygen profiles in the whole water column at a higher vertical resolution. Using a conductivity, temperature and depth (CTD) probe (RINKO CTD profiler with an optical fast DO sensor, JFL
Advantech Co. Ltd., Tokyo, Japan), we alternately measured the temperature and DO profiles at the
two lake extremities in the proximity of the LS-N and LS-S stations several times throughout the day.
Similarly, consecutive DO profiles were measured in the proximity of the LS-N stations on the 10th,
16th and 18th of April 2018.

133

134 **2.3 Numerical models**

In this study we used two numerical models to evaluate dynamic aspects of the measured internal oscillations. Therefore, we quantified the temporal evolution of the periodicity and the spatial structure of the free modes in Lake Iseo.

During the first stage, following the approach pursued in Guyennon et al. (2014) for Lake Como, a 138 modal analysis was performed to quantify the temporal evolution of the free modes periods. This 139 model subdivides a lake into constant density layers and provides the free baroclinic oscillations of 140 141 the layers interfaces by solving an eigenvalue problem (details are in Guyennon et al., 2014). The Lake Iseo bathymetry was discretized using a 160 m \times 160 m horizontal grid, while the horizontally 142 143 averaged vertical density profile was discretised monthly with the number of layers ranging from 2 to 4, as detailed in Table 2. As is typical for the subalpine deep lakes, beginning in April, a pronounced 144 145 3-layers thermal stratification develops, characterized by a well-mixed and warm surface layer, separated from the cold hypolimnion by an intermediate metalimnion. Under this condition, the upper 146 interface of the metalimnion (Z_2 in Table 2) was set at the depth of the maximum temperature gradient 147 (thermocline), while the lower interface (Z₃ in Table 2) was set at a depth of 35 m, below which the 148 vertical temperature gradient strongly weakens. Typically, stronger thermal stratification occurs 149 during August. After the thermocline deepening during the cooling period, the thermal stratification 150 reduces to two layers during winter, separated by one interface between 35 and 55 m and 151 characterized by a weak thermal gradient, which finally disappears during March. The thermal 152 stratification of Lake Iseo is also superimposed by a chemical stratification. Accordingly, we 153 considered an additional deep layer separated from the hypolimnion by the chemocline at 95 m depth 154 (Z₄ in Table 2), which is characterized by a 25 mg L^{-1} step in density because of the higher 155 concentration of dissolved salts. This value was quantified based on the chemical analysis of two 156 water samples collected at 40 m and 200 m depth, according to the procedure proposed by Boehrer 157 et al. (2010) (details are in Scattolini, 2018). The resulting discrete density structure well describes 158 the density profiles computed from the conductivity and temperature profiles (see Figure 2c). 159

The vertical and horizontal structure of the free modes were investigated in detail by using a three-160 dimensional (3D) hydrodynamic model that accounts for the non-linear terms of the momentum 161 equations. We used of the hydrostatic version of the Hydrodynamic-Aquatic Ecosystem Model 162 (AEM3D, Hodges and Dallimore, 2016). This model was developed from the ELCOM-CAEDYM 163 model (Hodges et al. 2000) and has already been successfully tested in simulating the internal wave 164 activity in the upper 50 m of Lake Iseo (Valerio et al., 2017). In particular, we investigated the wind-165 induced oscillations at approximately 100 m depth, using a vertical grid of 150 layers, 1 m in 166 thickness, followed by layers with gradually increasing thickness up to 25 m for the deepest part of 167 168 the lake. We also refined the uniform horizontal grid up to 80 m \times 80 m to better describe the bathymetry in the southern and northern areas. Finally, we used a passive tracer to follow the wind-169 driven vertical fluctuations in the oxycline. To simulate the structure of each single mode of 170 oscillation, we conducted numerical experiments in which the lake was forced by a synthetic 171 sinusoidal wind time series, with a maximum amplitude of 5 m s⁻¹, whose spatial and temporal 172 structure fits that predicted by the eigenmodel for the free oscillation modes. This approach was 173 174 already successfully applied by Vidal et al. (2007) to the study of the higher vertical modes of Lake 175 Beznar.

176

177 **3. Results**

178 **3.1 Analysis of the measured data**

The oscillatory motions measured around the thermocline and the oxycline show marked differences in periodicities and amplitudes. These differences clearly stand out from the comparison of the 12° C isotherm oscillation at LS-N (see Fig. 3a) and the 0.5 mg DO L⁻¹ oscillation at LS-S (see Fig. 3c). To better analyse the frequency content of these time series we used the wavelet analysis. We applied the Morlet transform to the two measured signals that, unlike the classical Fourier transform, allows localization of the signals both in frequency and time rather than in the frequency space only (Torrence and Compo, 1998).

Figure 3b highlights the strong concentration of the energy of the shallower oscillations for an approximately 1-day period during the thermally stratified period. The cooling period is characterised by higher energy peaks, with maximum values during November. A trend towards a longer period is also detectable. Conversely, the deeper DO oscillations (Fig. 3d) show higher energy content with a period ranging from 1 to 4 days during the observational phase: the first two months (Aug–Sept) are characterized by a stronger thermal stratification and four major peaks are detectable in the 2–4 days band; during the following two months (Oct–Nov), during the autumn cooling, the energy level is
lower and is centred at approximately 1 day; during the final two months (Dec–Jan), when the thermal
stratification is weak, the energy peaks maximize and are sparse in the 2–4 days band.

To better highlight these different behaviours, we individually show an analysis of a representative 195 196 fraction of each of these periods in Figures 4 to 6, respectively. Figure 4 shows the third week of October when the oscillatory motions at the depth of the thermocline and of the oxycline have energy 197 peaks centred around a daily period (see Figure 3). During this week, the wind speed and direction 198 show a typical pattern of the pre–alpine lakes (Valerio et al., 2017), blowing regularly from the south 199 200 during the day and the north during the night. The internal wave response in the upper 30 m is a 201 regular daily motion with an amplitude around of approximately 6 m. Deeper in the water, the main 202 vertical fluctuations at LS-S show a similar response both in terms of amplitude and periodicity, even though they are less regular and superimposed to higher frequency signals. The 0.5 mg L^{-1} iso-oxygen 203 204 at 95 m depth at LS-S is dominated by a 1-day period wave oscillation in counterphase with respect 205 to the 15 °C isotherm at the other end of the lake, suggesting a H1V1 behaviour (see Fig. 4e).

On the 21st and 22nd of July 2017, when a similar situation dominated by a V1H1 mode was present, we measured several temperature and oxygen vertical profiles around the thermocline and the oxycline at the LS-N and LS-S stations to better understand the vertical structure of this motion (see Figure 7). One can easily see that the downwelling that characterises the epilimnetic waters at LS-N is also present in the deeper layer of the oxycline, although it is vertically amplified and has a more irregular behaviour. A similar structure characterises the simultaneous upwelling at the LS-S station.

A completely different oscillatory response developed during the period 28/8–7/09 2017, when the 212 continuous wavelet transform highlights the different frequency content of the upper and deeper 213 motions (Fig. 5). Consistently, the temperature and oxygen contours at the different depths appear to 214 215 be decoupled. The upper 35 m (Fig. 5c) shows the superimposition of a dominant 1-day V1H1 oscillation and a lower amplitude, longer period (approximately 3 days), second vertical (V2) 216 217 oscillation mode. The latter is qualitatively evident in Figure 5c after a strong northerly wind started on the 1th of September, inducing a distinctive metalimnion widening on the 2nd of September, 218 followed by a metalimnion narrowing on the 3rd of September. Low-pass filtering of the 12°C 219 oscillations with an ~ 1-day and ~ 3-day cut-off period resulted in average amplitudes of 3.3 and 2.2 220 m, respectively. Deeper in the water (see Fig. 5d), the internal wave field is instead dominated by 221 much larger excursions of the oxycline (up to 20 m) and longer periodicities. Low-pass filtering of 222 the 0.5 mg L^{-1} iso-oxygen line at LS-S shows that the main oscillation pattern resembles the 223 superimposition of an ~ 3-day period oscillation with an average 14.6-m amplitude and a daily 224

oscillation with an average 2.2–m amplitude. The observed lower frequency motion presents a V2H1
structure, as shown in Figure 5e where the ~ 3–day oscillation of the DO immediately above the
oxycline is in counterphase at LS-N and LS-S. Figure 5c-d also show that the metalimnion widening
at LS-N (e.g. on the 2nd of September), associated with a downwelling in the hypolimnion,
synchronously occurs with a hypolimnetic upwelling at LS-S. Accordingly, during the period under
consideration, the field data suggest the dominance of a V1H1 mode in the epilimnion and a V2H1
mode in the hypolimnion.

From the 16th to the 18th of April 2018, when a similar situation dominated by V2H1 was observed 232 in the hypolimnion, we measured vertical profiles to examine the vertical structure of this motion at 233 a higher spatial resolution. The DO time series measured at LS-N and LS-S at the oxycline depth (see 234 235 Fig. 8a) shows a distinctive H1 oscillation with a period of approximately 4 days. In correspondence to the maximum and minimum vertical excursion of this fluctuation, we compared the vertical 236 237 temperature and oxygen profiles at LS-N around the thermocline and the oxycline, respectively. In 238 contrast to that shown in Figure 7, the oscillation is not vertically uniform: a downwelling of the thermocline on the order of a few meters is associated with an upwelling of the oxycline of 239 240 approximately 25 m. Accordingly, these data further highlight the amplification of the vertical excursion of the V2H1 motion in the oxycline area. 241

In comparison to the previous oscillations, an intermediate case is shown in Figure 6. In this case, 242 243 during winter of 2017, the water column is weakly thermally stratified and the wind blows mostly from the south (see Fig. 6b). The wavelet transform of the DO measurements at LS-S show a first 244 tight peak at an approximately ¹/₄-day⁻¹ frequency and a second at an approximately ¹/₂-day⁻¹ 245 frequency (see Fig. 3d). Consistently, the time series of the 0.3 mg DO L⁻¹ measured at LS-S (see 246 Fig. 6d) shows evidence of both a shorter and a longer period signal. Filtering with the cut-off periods 247 248 highlighted in the spectrum show that these ~ 2 and ~ 4 -day signals have in this case comparable amplitudes (5.0 and 7.6 m, respectively) around the chemocline at LS-S. At LS-N, the DO time series 249 250 at 85 m depth oscillates in counter phase with respect to the southern series with coherent periodicities and amplitudes, so suggesting an H1 response (see Fig. 6d). 251

252

3.2 Analysis of the model results

With reference to the modal results, Table 2 reports the monthly averaged values used for the calculations, and the obtained yearly evolution of the periods of the V1H1, V2H1 and V3H1 modes. During April, all the periods present values (V1H1: 2.9, V2H1: 4.6 and V3H1: 6.4 days) that progressively decrease during the warming season. During the strongly stratified period (July– October) the modelled of V1H1, V2H1 and V3H1 periods show nearly constant values, of approximately 1, 3 and 4 days, respectively. As soon as the water column starts cooling and the thermocline deepens, all mode periods start increasing. During the weaker 3–layer stratification during February, when a similar density difference is present across the metalimnion and chemocline, V2H1 reaches a 7.4–day period, while the V1H1 period increases up to 3.3 days during March, when the water column is thermally homogeneous and only a saline stratification is present.

264 Regarding the spatial structure of these modes, Table S1 (see the supplementary material attached to 265 this paper) summarizes the 3D results in terms of maximum interface displacements at different lake locations during four representative periods of the year. In the following, we mostly focus on the 266 267 V1H1 and V2H1 oscillations of the thermocline (ξ_2) and the chemocline or oxycline (ξ_4) at LS-S and LS-N to provide an interpretation of the data measured at these stations from July 2017 to February 268 2018. Regarding the first vertical mode, all the interfaces oscillate in phase at the different depths. At 269 LS-N (220 m depth), their amplitude is nearly vertically uniform ($\xi_4/\xi_2 \approx 1$), while at LS-S and NB 270 271 (105 m depth) the intermediate and deep tilt is amplified ($1.2 < \xi_4 / \xi_2 < 2.3$). Conversely, the deep 272 interface tilt is strongly damped and more irregular in the eastern basin, a 100-m flat plateau located 273 east of Monte Isola ($\xi_4/\xi_2 \approx 0.4$). In absolute terms, the weaker is the density stratification, the stronger 274 is the interface tilt. At the end of winter, when the water column is thermally homogenous and chemically stratified, the V1H1 amplitudes are up to 7.5 times larger than those during summer. 275 Regarding the second vertical mode, the interfaces oscillation is strongly non-uniform over the 276 vertical, with the metalimnion and the chemocline both oscillating in counterphase with respect to 277 the upper thermocline and with much larger vertical displacements. At LS-N, the vertical 278 displacement of the chemocline is on average 2.6 times larger than that of the thermocline. This 279 vertical amplification is favoured by larger density gradients (at LS-N ξ_4/ξ_2 decreases from 3.4 during 280 August to 1.8 during December). Similarly to that observed for V1H1, this vertical amplification is 281 also enhanced at the southern end of the lake (average $\xi_4/\xi_2 = 4.0$ at LS-S), while it is strongly 282 283 attenuated in the eastern basin, where the chemocline oscillations are more irregular in time and show maximum vertical displacements comparable to those of the thermocline $(\xi_3/\xi_1 \approx 1)$. We emphasize 284 that, independent from the vertical mode and stratification, the ratio between the V1H1 and V2H1 285 amplitude of a given interface simulated at different lake locations does not present a wide range of 286 variation. In particular, the displacement of the deeper interface ξ_4 at the different locations is as 287 follows: $0.6 < \xi_{4-LS-N} / \xi_{4-LS-S} < 0.8$; $0.1 < \xi_{4-EB} / \xi_{4-LS-S} < 0.2$; $0.7 < \xi_{4-NB} / \xi_{4-LS-S} < 1.2$. This implies that the 288 289 chemocline mantains a similar H1 horizontal structure throughout the year, even with different absolute values depending on the stratification and the vertical mode (see Fig. S1 in thesupplementary material).

The obtained numerical results clarify the nature of the observed oscillations and extend the spatial 292 293 information provided by the local measurements. Between October and November (see Fig. 4), we 294 observed a daily, coupled oscillatory response at the chemocline and thermocline. During this time, 295 the natural period of V1H1 is daily as well, confirming that the whole water column is dominated by 296 this type of motion. This is consistent with the observed spatial structure characterized by a counterphase response at the two lake ends (H1) and a similar amplitude at the different depths (V1). During 297 298 the strongly stratified period (Aug-Sept), we occasionally observed a decoupled internal wave response at the different depths (see Fig. 5). By comparing the periodicity of the measured oscillations 299 300 and that of the unforced modes (see Fig. 3), the thermocline appears to be dominated by a V1H1 motion (~ 1-day period), while the oxycline is dominated by a V2H1 motion (~ 2-3-day period). 301 302 This suggests that both modes were excited by the wind, but at different energy levels along the water 303 column. This decoupled response can be explained by the vertical structure of the modes detailed in 304 Table S1. During the summer stratification, the V1H1 amplitudes are nearly vertically uniform (1.1 $< \xi_4/\xi_2 < 2.3$). Conversely, the V2H1 amplitude at the chemocline ξ_4 is up to 5.7 times larger than that 305 of the thermocline ξ_2 . Accordingly, when a second vertical mode is excited by the wind, the larger 306 307 vertical displacements occur at the deeper interface. This vertical amplification may explain why the V2H1 mode is dominant in the deeper waters and is in contrast weaker than the V1H1 daily signal 308 309 around the thermocline. Finally, during the period from December to January (see Fig. 6) we observed the superimposition of ~2-days and ~4-days large oscillations at the oxycline depth. According to 310 311 the periodicities of the unforced modes, they correspond to a V1H1 and V2H1 modes, respectively 312 (see Fig. 3e). The evidence of a large amplitude V1H1 mode at this depth is consistent with the 313 increased displacements reported in Table S1 corresponding with the weaker density stratification.

Valerio et al. (2012) showed that the internal wave modes in the upper water layers are excited 314 whenever the spatial and temporal structure of a wind field over a lake matches the surface velocity 315 316 field of a particular internal mode. Accordingly, as shown in Figure 3e, we superimposed the natural 317 frequencies of the two main vertical modes with the continuous wavelet transform of the northerly components of the wind forcing, to assess whether a fit in their periodicies might explain the observed 318 internal wave motions. During the stratified period (July-November), most of the wind energy 319 oscillates at a period of approximately 1 day, likely because of the regular alternation of northerly 320 and southerly thermal winds, typical of the area (see Valerio et al. 2017). This forcing perfectly fits 321 322 the V1H1 mode that is regularly excited and dominates the response of the upper waters (see Fig. 3b).

Occasionally, the daily wind energy reduces its intensity when the wind blows longer from the same 323 direction. From July to October 2017, this occurred three times (see Fig. 3e). Interestingly, 324 corresponding to each of these events, there is a large energy peak in the oxycline oscillations for the 325 lower frequencies (see Fig. 3d). The reason is a resonance between the wind and the waves: the longer 326 periodicity of the wind forcing approaches the natural periodicity of the V2H1 mode, such that it is 327 excited in place of V1H1, inducing large vertical fluctuations below the metalimnion. During the 328 weakly stratified period, the thermal conditions in the surrounding watershed limit the intensity and 329 330 the regularity of the alternating thermal winds, causing a spread of wind energy over a larger band of 331 frequencies (see Fig. 3e). In contrast to that which occurred prior, this condition favours the excitation 332 of a longer period V1H1 oscillation that clearly is also evident at the oxycline depth, with amplitudes 333 favoured by the weak stratification.

334

335 4. Discussion and Conclusions

In Lake Iseo reduced deep mixing has resulted in the formation of an anoxic monimolimnion below 95 m depth, such that any vertical displacement of the oxycline may induce variation in redox conditions of the contiguous sediments. Accordingly, it seems reasonable to advance the hypothesis that the internal wave motions in Lake Iseo might result in unstable unsteady sediment–water fluxes.

The data collected from July 2017 to February 2018 clearly support our initial hypothesis that there 340 are large and periodic displacements of the oxycline. The typical oxycline oscillation in the southern 341 basin is in the range of 10 - 20 m, with periods ranging from 1 to 4 days. Comparing these movements 342 to those already studied in the lake's upper water layers (Valerio et al. 2012), dominated to a large 343 extent by a 1- day motion, we found the dynamics in the deeper waters to be more irregular in 344 character, featuring larger amplitudes at lower frequencies. We primarily attributed this behaviour to 345 the excitation of a V2H1 mode characterized by amplified vertical displacements below the 346 thermocline. During weakly stratified conditions this behaviour was explained by the excitation of a 347 V1H1 mode, featuring lower frequencies and larger tilts because of the weaker density gradients. In 348 349 both cases, the overlap of the temporal structure of the wind forcing with that of the two modes provides evidence for a resonant response to wind as observed, inter alia, by Vidal et al. (2007). 350

A primary role for the excitation of these deep internal wave motions is played by the permanent chemical stratification. In Lake Iseo, the decomposition of organic matter and the dissolution of its end products have favoured the solutes accumulation in the deeper waters since the 1980s. Accordingly, a stable density gradient is present between the oxic mixolimnion and the anoxic monimolimnion, contributing to maintaining the latter isolated from the water above. This condition allows for the occurrence of large baroclinic motions at the interface of these layers, even if the water column is thermally homogenous. Accordingly, this work provides experimental and numerical evidence of a chemical gradient supporting deep baroclinic motions in perennially stratified lakes, as already numerically argued by Salvadé et al. (1988) in Lake Lugano, where a similar density stratification occurs.

The observations of highly energetic V2H1 motions in Lake Iseo broaden the observations of higher 361 vertical modes, which have been much less frequently reported in lakes with respect to the first 362 363 vertical mode (e.g. Wiegand and Chamberlain, 1987; Münnich et al. 1992, Roget et al., 1997), and rarely reported in deep lakes (e.g. Boehrer 2000; Boehrer et al. 2000; Appt et al. 2004; Guyennon et 364 365 al. 2014). Interestingly, stronger evidence of these motions in the deep waters compared to the upper waters supports the idea by Hutter et al. (2011) that the reason for rare documentation in the literature 366 367 of these motions is not because they are not excited but that the measuring techniques usually are not sufficiently detailed to capture them. Moreover, if typically their excitation is seen to be favoured by 368 369 the presence of a thick metalimnion, in this case they are enhanced by the presence of a chemical 370 stratification in the deeper waters. Conducting a sensitivity analysis on the density stratification used as the initial condition for the simulations, we observed, e.g. during August, that the amplitude of the 371 second vertical modes is from 2 to 3 times greater compared to a case where the chemical stratification 372 is absent. Interestingly, similar observations of higher baroclinicity supported by deep isopycnal 373 layers have been observed in other environments in corresponding to vertical salinity gradients (South 374 Aral Sea by Roget et al. 2017) and turbidity (Ebro Delta by Bastida et al., 2012). 375

376 The observation of a pronounced spatio-temporal oxycline dynamics supports the hypothesis of the 377 occurrence of alternating redox conditions in the water above the sediments at the bottom of Lake 378 Iseo. For example, considering the variations in DO concentration at 95 m of depth in the (d) panels of Figures 4 to 6, one can observe that the sediment surface at this depth is periodically forced by a 379 variation in DO concentrations in the overlying water between 0 and 3 mg L⁻¹. To quantify the 380 potential biogeochemical implications of the oxycline dynamics in Lake Iseo, it is important to 381 382 estimate the areal extent of sediment subjected to alternating redox conditions. Obviously, the smaller the bed slope, the larger the sediment area impacted by a given vertical oxycline displacement. 383 384 Accordingly, areas subjected to alternating redox conditions will mainly be located in the northern, 385 southern and eastern sub-basins (see Fig. 9a), where the bottom more gradually rises compared to 386 that of the central basin. The depth-area relationship of the three sub-basins (see Fig. 9a) shows that approximately 5 km² of sediment area is situated between the depths of 85 and 115 m, representing 387

the upper limit of the area subjected to episodic changes in oxygen availability. However, a more 388 precise calculation requires knowledge of the spatial pattern of the oxycline oscillations in the three 389 sub-basins. To this end, we coupled the area-depth curve of the southern basin to the time series of 390 vertical displacements of the 0.5 mg DO L⁻¹ iso-oxygen line at LS-S, taken as a reference for the 391 oxycline depth. The same analysis was extended also to the northern and eastern basins, where we 392 used the spatial distribution of the deeper layer interface provided by the 3D numerical model to 393 estimate the oxycline oscillations (see Table S1). The resulting basin-specific areas subjected to 394 alternating redox conditions (typically with variations higher than $1 \text{ mg } L^{-1}$) are shown in Figure 9b. 395

We estimated that, overall, 1.9 km² of bottom sediments of Lake Iseo, 3% of the whole area, are on 396 average subjected to alternating redox conditions with periods of from 1 to 4 days, with a maximum 397 398 areal extent during summer, when long-lasting winds favour the excitation of a second vertical mode, and from January to February, when the weak thermal gradients favour strong tilts in the chemocline. 399 400 The relative contributions of the sub-basins to the whole area subjected to alternating redox conditions 401 are 49% (southern basin), 32% (northern basin) and 19% (eastern basin). Because of its conformation as a horizontal plateau with a typical depth of 100 m, the eastern basin contributes only if the oxycline 402 is above 100 m depth. 403

Oxycline dynamics affect lake sediments with implications for the redox-controlled biogeochemical 404 405 processes therein. Redox-sensitive P release (Søndergaard, 2003) may be halted in sediment depth 406 segments affected by oxycline oscillations and shift P towards redox-insensitive fractions (Parsons et al., 2017). However, the role of sediments as sink and source of P is known to be controlled by a suite 407 diagenetic processes including P supply, microbial mineralization, and interaction between iron and 408 409 sulphur (Hupfer and Lewandowski, 2008). The susceptibility of these processes to excursion in oxygen availability is less well understood. According to our calculations, an additional 3% of the 410 sediment area is affected by such excursions. The monimolimnion of Lake Iseo stores the vast 411 majority of the in-lake P (360 t of 480 t, April 2016, Lau et al., in preparation), indicating the relevance 412 413 of P release from sediment below the oxycline. Therefore, it remains crucial to further explore the dynamics in redox forcing in sediments of perennially stratified lakes and the entailing implications 414 for internal P cycling and biogeochemical turnover. 415

416

417 **Competing interests**

418 The authors declare that they have no conflict of interest.

420 Acknowledgments

- 421 This research is part of the ISEO (Improving the lake Status from Eutrophy to Oligotrophy) project
- and was made possible by a CARIPLO Foundation grant number 2015-0241. Support from the
- 423 Deutsche Forschungsgemeinschaft to MPL (LA 4177/1-1) is gratefully acknowledged. We would
- 424 like to thank our IGB colleagues Sylvia Jordan, Tobias Goldhammer, Thomas Rossoll, and Eric
- 425 Hübner for their support during the sampling campaigns.

427 **References**

- Appt J., Imberger J., and Kobus H.: Basin-scale motion in stratified Upper Lake Constance, *Limnol. Oceanogr*, 4, 919-933, 2004.
- Bastida, I., Planella, J., Roget, E., Guillen, J., Puig, P., and Sanchez, X.: Mixing dynamics on the
 inner shelf of the Ebro Delta, Sci. Mar., 76, 31–43, 2012.
- Bernhardt, J., Kirillin, G. and Hupfer, M.: Periodic convection within littoral lake sediments on
 the background of seiche-driven oxygen fluctuations. *Limnol. Oceanogr.*, 4, 17–33, 2014.
- Boehrer, B.: Modal response of a deep stratified lake: western Lake Constance. *J. Geophys. Res.*,
 105(C12), 28837–28845, 2000.
- Boehrer, B., Ilmberger, J., and Münnich, O.: Vertical structure of currents in Western Lake
 Constance. J. Geophys. Res., 105: 28823–28835, 2000.
- Boehrer, B., Herzsprung, P., Schultze, M., Millero, F.J.: Calculating density of water in
 geochemical lake stratification models. *Limnol. Oceanogr. Methods*, 8, 567–574, 2010.
- Brand, A., McGinnis, D. F., Wehrli, B. and Wüest, A.: Intermittent oxygen flux from the interior
 into the bottom boundary of lakes as observed by eddy correlation. *Limnol. Oceanogr.*, 53, 1997–
 2006, 2008.
- Bryant, L. D., C. Lorrai, C., McGinnis, D. F., Brand, A. Wüest, A., and Little, J. C.: Variable
 sediment oxygen uptake in response to dynamic forcing. *Limnol. Oceanogr.*, 55, 950–964, 2010.
- Chowdhury, M. R., Wells, M. G., and Howell, T.: Movements of the thermocline lead to high
 variability in benthic mixing in the nearshore of a large lake, *Water Resour. Res.*, 52, 3019–3039,
 2016.
- Deemer, B. R., Henderson, S. M. and Harrison, J. A.: Chemical mixing in the bottom boundary
 layer of a eutrophic reservoir: The effects of internal seiching on nitrogen dynamics. *Limnol. Oceanogr.*, 60, 1642–1655, 2015.
- Garibaldi, L., Mezzanotte, V., Brizzio, M.C., Rogora, M., Mosello, R.: The trophic evolution of
 Lake Iseo as related to its holomixis. *Journal of Limnology*, 62: 10–19, 1999.
- Guyennon N., Valerio, G., Salerno, F., Pilotti, M., Tartari, G., Copetti, D.: Internal wave weather
 heterogeneity in a deep multi-basin subalpine lake resulting from wavelet transform and numerical
 analysis, *Advances in Water Resources*, 71, 149-161, 2014.

- 456 Hodges, B.R., Dallimore, C.: *Aquatic Ecosystem Model: AEM3D*, v1.0, User Manual.
- 457 Hydronumerics. Australia, Melbourne., 2016.

Hodges, B.R., Imberger, J., Saggio, A., and Winters, K. Modeling basin-scale internal waves in a
stratified lake. *Limnol. Oceanogr.*, 45: 1603–1620, 2000.

- 460 Hupfer, M., and Lewandowski, J.: Oxygen Controls the Phosphorus Release from Lake
- 461 Sediments a Long-Lasting Paradigm in Limnology. *International Review of Hydrobiology*, 93:
- 462 415-432. doi:10.1002/iroh.200711054, 2008.
- Hutter, K., Wang, Y., and Chubarenko, I. P. (Eds.): *Physics of Lakes: Lakes as Oscillators*,
 Springer-Verlag, Berlin, Germany, 2011.
- Imberger , J. : Flux paths in a stratified lake: A review. In J. Imberger [ed.], *Physical processes in lakes and oceans*. American Geophysical Union, 1–18, 1998.
- Imboden, D. M., and Wüest, A.: Mixing mechanisms in lakes, in *Physics and Chemistry of Lakes*, edited by A. Lerman, D. Imboden, and J. Gat, pp. 83 138, Springer-Verlag, New York,
 1995.
- Jørgensen, B. B., and Marais, D. J. D.: The diffusive boundary-layer of sediments: Oxygen
 microgradient over a microbial mat. *Limnol. Oceanogr.*, 35, 1343–1355, 1990.
- Kirillin, G., Engelhardt, C. and Golosov, S.: Transient convection in upper lake sediments
 produced by internal seiching. *Geophys. Res. Lett.* 36, L18601, 2009.
- 474 Lau, M., Valerio, G., Pilotti, M., and Hupfer, M.: Meromictic waters store phosphorus better475 than sediments. *In preparation*.
- Lorke A., Müller B., Maerki M., and Wüest, A.: Breathing sediments: The control of diffusive
 transport across the sediment-water interface by periodic boundary-layer turbulence. *Limnol. Oceanogr.*, 48, 2077–2085, 2003.
- 479 Lorke, A., Peeters, F., and Wüest, A.: Shear-induced convective mixing in bottom boundary
 480 layers on slopes, *Limnol. Oceanogr.*, 50, 1612–1619, 2005.
- 481 Lorke, A., and Peeters, F.: Toward a Unified Scaling Relation for Interfacial Fluxes. *J. Phys.*482 *Oceanogr.*, 36, 955–961, 2006.
- Moreira S., Schultze M., Rahn K., and Boehrer B. 2016. A practical approach to lake water density
 from electrical conductivity and temperature. *Hydrology And Earth System Sciences*, 20, 2975-2986.

Münnich, M., Wüest, A., and Imboden, D. M.: Observations of the second vertical mode of the
internal seiche in an alpine lake. *Limnol. Oceanogr.*, 37, 1705–1719, 1992.

Parsons, C. T., Rezanezhad, F., O'Connell, D. W., and Van Cappellen, P.: Sediment phosphorus
speciation and mobility under dynamic redox conditions, Biogeosciences, 14, 3585-3602,
https://doi.org/10.5194/bg-14-3585-2017, 2017.

490 Pilotti, M., Valerio, G., and Leoni, B.: Data Set For Hydrodynamic Lake Model Calibration: A
491 Deep Pre-Alpine Case, *Water Resources Research*, 49, 7159–7163. 2013.

Roget, E., Khimchenko, E., Forcat, F., and Zavialov, P.: The internal seiche field in the changing
South Aral Sea (2006–2013), *Hydrol. Earth Syst. Sci.*, 21, 1093-1105, https://doi.org/10.5194/hess21-1093-2017, 2017.

Roget, E., Salvadé, G., Zamboni, F.: Internal seiche climatology in a small lake where
transversal and second vertical modes are usually observed, *Limnology and Oceanography*, 42,
1997.

498 Salvadé, G., Zamboni, F., and Barbieri, A.: 3-layer model of the north basin of the Lake of
499 Lugano, *Ann. Geophys.*, 6, 463–474, 1988.

Scattolini S.: *Determinazione di un'equazione di stato per le acque del lago d'Iseo*. Batchelor
Thesis, Università degli Studi di Brescia, Brescia, Italy. 2018.

Søndergaard, M., Jensen, J.P., and Jeppesen, E.: Role of sediment and internal loading of
phosphorus in shallow lakes, Hydrobiologia, 506: 135. 2003.

Torrence, C., Compo G.P.: A practical guide to wavelet analysis. *Bull Am Meteorol Soc*, 79:61–
78. 1998.

Valerio, G., Pilotti, M., Marti, C.L., and Imberger J.: The structure of basin scale internal waves
in a stratified lake in response to lake bathymetry and wind spatial and temporal distribution: Lake
Iseo, Italy. *Limnol. Oceanogr.*, 57(3), 772-786. 2012.

Valerio, G., Cantelli, A., Monti, P., and Leuzzi, G.: A modeling approach to identify the
effective forcing exerted by wind on a pre-alpine lake surrounded by a complex topography. *Water Resources Research*, 53(5), 4036–4052, 2017.

Vidal, J., Rueda, F.J., and Casamitjana, X: The seasonal evolution of vertical-mode internal
waves in a deep reservoir. *Limnol Oceanogr.*, 52, 2656–67. 2007.

514 Wiegand, R.C., and Chamberlain, V. Internal waves of the second vertical mode in a stratified
515 lake, *Limnol. Oceanogr.*, 32 (1), 29-42, 1987.

Table 1. Overview of the oxygen measurements in Lake Iseo (sampling frequency of 60 s⁻¹).

522	ID	Station	Depth	Distance from	Investigated period			
			(m)	the bottom (m)				
523	SO85	LS-S	85	20	21/07/2017 - 18/04/2018			
524	SO90	LS-S	90	15	21/07/2017 - 18/04/2018			
525	SO95	LS-S	95	10	21/07/2017 - 18/04/2018			
525	SO105	LS-S	105	0	21/07/2017 - 18/04/2018			
526	NO85	LS-N	85	135	24/10/2017 - 16/04/2018			
	NO95	LS-N	95	127	22/07/2017 - 24/10/2017			

Table 2. Features of the first horizontal, first, second and third vertical modes in Lake Iseo during a 528 one year period. The monthly-averaged layered structure used for the calculation includes the depth Z_i of the upper interface of each ith layer, and its density difference with respect to the deepest layer, ρ_{i} . ρ_{4} .

			Layere	ed structi	Periods of the H1 modes					
	Z ₂	Z ₃	Z_4	ρ1-ρ4	ρ2-ρ4	ρ3-ρ4	V1	V2	V3	
Time	e (m)				(kgm ⁻³)			(hours)		
Jul-17	12.5	35.0	95.0	1.700	0.223	0.029	26.7	65.1	88.9	
Aug-17	15.0	35.0	95.0	1.741	0.204	0.03	24.1	60.3	90.3	
Sep-17	17.5	35.0	95.0	1.486	0.187	0.031	23.7	65.4	92.5	
Oct-17	20.0	35.0	95.0	1.049	0.192	0.032	25.9	69.2	94.1	
Nov-17	22.5	35.0	95.0	0.645	0.187	0.034	31.0	74.4	102.8	
Dec-17	35.0	-	95.0	0.214	0.032	-	43.8	82.3	-	
Jan-18	45.0	-	95.0	0.059	0.028	-	67.7	139.2	-	
Feb-18	55.5	-	95.0	0.046	0.027	-	71.2	177.3	-	
Mar-18	-	-	95.0	0.025	-	-	78.5	-	-	
Apr-18	7.5	35.0	95.0	0.200	0.071	0.027	69.3	112.3	153.5	
May-18	10.0	35.0	95.0	0.596	0.107	0.028	48.4	75.8	108.7	
June-18	12.5	35.0	95.0	1.072	0.131	0.028	33.6	69.1	101.3	



Figure 1. Contour of Lake Iseo bathymetry and isodepth lines at 30 m spacing . The black dots show the measurement stations located on the shore (SS) and in the lake (LS), both north and south. The red squares indicate the two points at 98 m depth in the eastern basin (EB) and 105 m in the northern basin (NB) that are mentioned in the text.



Figure 2. (a) Vertical profile of temperature-compensated conductivity (EC25) and dissolved oxygen 542 (DO) measured on 10/04/2018 at LS-N. (b) Vertical profile of temperature (T) and dissolved oxygen 543 (DO) measured on 22/07/2017 at the LS-N. The circles and the crosses show the DO sensors at LS-544 S and LS-N, respectively. The dots and the squares show the depth of the temperature sensors at LS-545 N, with the squares indicating the high-accuracy sensors. (c1-c4) Vertical profiles of monthly 546 averaged density (solid lines) during four months and the corresponding discrete layered structure 547 (dashed line) used in the modal model. The density profiles were calculated on the basis of an 548 empirical equation of state that relates density to conductivity and temperature, calibrated for lake 549 550 Iseo according to the algorithm by Moreira et al. (2016) (details are in Scattolini, 2018).



Figure 3. (a) Time series of the vertical displacements of the 12°C isotherm (white line) measured at 553 554 LS-N, superimposed on the interpolated temperature distribution between 0 and 40 m, and (b) the associated continuous wavelet transform for the period between the 23rd July and 21st of 555 November 2017. (c) Time series of the vertical displacements of the 0.5 mgDO L⁻¹ isoline measured 556 at LS-S, superimposed on the interpolated distribution of oxygen, and (d) the associated continuous 557 wavelet transform. (e) Natural periods of the V1H1, V2H1, and V3H1 modes superimposed on the 558 continuous wavelet transform of the N-S component of the wind measured at LS-N. The grey shaded 559 regions on either end indicate the cone of influence, where edge effects become important. The three 560 rectangles with a black outline show the three periods analysed in the following Figures 4-6. 561



Figure 4. Time series measured from the 14th to 24th of October 2017 of (a) wind speed and its
southerly component and (b) wind direction at LS-N, followed by the spatial and temporal variation
in (c) temperature between 5 and 25 m depth at LS-N and of (d) DO between 80 and 105 m at LS-S.
Panel (e) compares the time series of DO measurements at the LS-N and LS-S stations.

568 Corresponding to each tick of the horizontal axis it is the time 00:00.



Figure 5. Same as Fig. 4 but referring to the period of 28 August – 07 September 2017.





Figure 6. Same as Fig. 4 but referring to the period 05 - 18 December 2017.



Figure 7. (a) DO concentration at 90 m depth recorded at station LS-N on the 21th of July 2017.
Coloured dots on the x-axis indicate the sampling time of the vertical profiles shown in the panels
(c-f). Panels (c) and (d) compare the profiles of temperature between 0 and 60 m, while panels (e)
and (f) compare the profiles of DO between 65 and 125 m. Red and blue colours refer to the
northern and southern sampling location (see panel b), respectively.



587

Figure 8. (a) Time series of DO measured at 85 m depth on April 2018. Red and blue lines refer to the northern and southern sampling location, respectively (see panel b). Coloured dots on the x-axis indicate the sampling time of the vertical profiles shown in panels (c-d). Panel (c) compares the profiles of temperature between 0 and 80 m depth at LS-N, while panel (d) compares the profiles of DO between 50 and 130 m at LS-N.



595

Figure 9. (b) Estimation of the area of the bottom sediments subjected to alternating redox conditions. 596 597 The areas were calculated by considering the oscillations of the oxycline over a 3-day long time window. The three colours make reference to the contribution of the southern (S, blue), northern (N, 598 red) and eastern basin (E, yellow), as shown on the map. In the left panel (a), the area-depth curves 599 indicate the cumulative area "a" of the bottom situated below a given water depth in the whole lake 600 (W) and in each sub-basin (E, N, S). On the x-axis, the area "a" was normalized with the total area 601 "A" of each basin. The grey shaded area marks the maximum and minimum vertical displacement of 602 the 0.5 mgDO L^{-1} recorded at LS-S, highlighting the area of the bottom where the oxycline fluctuates. 603