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# Dark production of hydroxyl radicals by aeration of anoxic lake water

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## Abstract

Lake circulation is an important phenomenon that ensures oxygenation of the water column. Here we report that aeration of anoxic hypolimnion water causes production of highly reactive hydroxyl radicals ( $\cdot\text{OH}$ ), which are also produced photochemically in the epilimnion. Model calculations suggest that the dark process of  $\cdot\text{OH}$  generation can be comparable with photochemical reactions in some lake environments, provided that the hypolimnion is a significant fraction of the whole lake volume. In these cases, lake overturn could significantly contribute to the yearly  $\cdot\text{OH}$  budget of the lake water and might cause significant degradation of some pollutants, for which the reaction with  $\cdot\text{OH}$  is an important removal process from surface waters.

**Keywords:** Hydroxyl radicals; Anoxic Lake Water; Lake Circulation; Reactive Oxygen Species.

## Introduction

Reactive transient species are photochemically produced in natural waters and they include the hydroxyl ( $\cdot\text{OH}$ ) and carbonate ( $\text{CO}_3^{\cdot-}$ ) radicals, singlet oxygen ( $^1\text{O}_2$ ) and organic matter triplet states. They play an important role in the degradation of pollutants and in the oxidative processing of natural organic matter, with important implications for the biogeochemical carbon cycle (Aarnos et al., 2012; Fenner et al., 2013; Remucal, 2014). The generated transients are produced photochemically in the surface water layer, upon sunlight irradiation of photosensitisers such as chromophoric dissolved organic matter and nitrate (Al Housari et al., 2010). Photochemical processes are limited or negligible in the lower depths of water bodies (Barbeau et al., 2001), including water in the lake hypolimnion during the stratification period(s). However, dark formation

of  $\cdot\text{OH}$  has been recently observed upon aeration of both humic acids, previously exposed to electrochemical reduction under anoxic conditions (Page et al., 2012), and anoxic groundwater (Page et al., 2013). Interestingly, a similar reduction process can be induced microbially in humic substances (Klöpffel et al., 2014). Such processes are intriguing because they do not require sunlight, and because they involve aeration of anoxic water. During summertime, lake water may be thermally stratified because the warmer water near the surface has lower density than the deeper and colder one. Under such conditions and depending on the surface productivity, the hypolimnion may become anoxic. This happens because oxygen is consumed by respiration and it might not be efficiently supplied by diffusion from the well-oxygenated upper layer or by photosynthesis (absent in the aphotic zone below the thermocline). Stratification usually lasts until the epilimnion temperature decreases, causing the lake to become isothermal and triggering circulation. Depending on the complete or partial overturn and on its frequency, lakes are distinguished as monomictic (a complete mixing occurs once per year), di/polymictic (two or more complete circulations occur per year) and meromictic (the overturn occurs only in a fraction of the water column and an unmixed layer can remain for years). A total overturn may be prevented by the excessive water density near the bottom, often because of accumulation of inorganic and organic substances with formation of stable chemoclines. In the presence of anoxic hypolimnion water, mixing ensures reoxygenation (Wetzel, 2001; Posch et al., 2012) and the contact between anoxic water and oxygen is a potential  $\cdot\text{OH}$  source. This paper explores the role of dark hydroxyl radical formation during aeration of anoxic lake water.

## Materials and Methods

Water was sampled in summer from the epilimnion and hypolimnion of stratified lakes located in NW Italy: Avigliana Grande (AV), Candia (CA), Viverone (VI) and Sottano della Sella (SdS). For additional information about the studied lakes see Table 1. The sampling zone was reached by boat and deep water was sampled with a Niskin bottle. The depth profiles of temperature, conductivity, dissolved oxygen and pH are reported in Figure 1. Water was anoxic below 5 m for CA (maximum depth 7 m), 15 m for AV (maximum depth 26 m), 20 m for VI (maximum depth 58 m) and 30 m for SdS (maximum depth 35 m). The lake surfaces had oxygen concentration at or even above saturation, due to the combination of contact with the atmosphere and photosynthetic activity. Some data concerning lake water characterisation are reported in Table 1. Complete data, including the main anions and cations, are provided as Supplementary Material (hereafter SM, Figures S1 to S3). For each lake, two samples were taken from the anoxic hypolimnion (0.5-2 m above the lake bottom, sampling points being at a horizontal distance of 50-200 m) and one sample from the epilimnion, approximately at middle (horizontal) distance between the hypolimnion sampling points.

The production of  $\cdot\text{OH}$  was determined with the transformation of terephthalic acid (TA) into hydroxyterephthalic acid (TAOH) as probe reaction. The formation yield of TAOH from TA upon reaction with  $\cdot\text{OH}$  has been reported as  $\sim 20\%$  at the temperature and pH conditions of the studied samples (Charbouillot et al., 2011). Because every five  $\cdot\text{OH}$  that react with TA, only one gives TAOH, one should multiply the TAOH data by five to get the  $\cdot\text{OH}$  formation. Page et al. (2012) used a different yield (35%), but Charbouillot et al. (2011) studied the TAOH yield as a function of pH and temperature and a 20% yield is compatible with the conditions of the lake water samples. Differences in the reported yields could be due to differences in the experimental temperatures.

Near-bottom anoxic water was collected, spiked with a terephthalic acid/terephthalate solution at similar pH as the lake water, and magnetically stirred in open amber flasks to allow aeration. The procedures used to protect the flasks from sunlight exposure and to quench the reaction between  $\cdot\text{OH}$  and TA are reported in the Materials and Methods section of SM. For each lake,  $\cdot\text{OH}$  formation was studied in two bottom samples (initially anoxic) and in one sample from the surface, and two replicas of each sample were made.

The importance of the studied dark process was assessed by comparison with photoinduced reactions. Epilimnion photochemistry was modelled with the APEX software (Aqueous Photochemistry of Environmentally-occurring Xenobiotics) (Bodrato and Vione, 2014). Modelling was based on photochemically relevant parameters of surface lake water (nitrate, DOC, inorganic carbon, pH, see Table 1) and on a reference depth that is representative of the epilimnion (see Figure 1; epilimnion depth was taken as 3 m for CA, 10 m for AV, 15 m for VI and 25 m for SdS).

## Results and Discussion

Figure 2 reports the TAOH time trend in the hypolimnion and surface samples for each studied lake (two replicas are reported for each aeration time, the curves are just guides for the eye). TAOH was already detectable after 10 min of contact time with the atmosphere and its concentration increased quite quickly in the first hour of the reaction, after which its further increase was more limited. The TAOH values detected at the longest reaction times ( $> 6$  h) were within  $0.3\text{--}1\ \mu\text{M}$  for lakes AV and VI, and below  $0.05\ \mu\text{M}$  for CA and SdS. At such reaction times, the oxygen saturation in the relevant samples was around 100%. The TAOH concentration in surface samples was always below  $0.01\ \mu\text{M}$ . This issue suggests, among other things, that aerobic biological processes are unlikely to determine an important transformation of TA into TAOH.

Figure 2 shows that dark  $\cdot\text{OH}$  production was much higher in hypolimnion than in epilimnion water. For the hypolimnion, the TAOH concentration was in the order  $\text{AV} > \text{VI} > \text{SdS} > \text{CA}$ . By dividing the longest-time TAOH concentration for the yield of the reaction  $\text{TA} + \cdot\text{OH} \rightarrow \text{TAOH}$  (Charbouillot et al., 2011), one gets the total formed  $\cdot\text{OH}$  that represents the moles per litre of  $\cdot\text{OH}$  produced by aeration of anoxic water. Note that this is not the concentration of  $\cdot\text{OH}$  at any time,

which would be much lower: the radical  $\cdot\text{OH}$  is formed and quickly reacts, but the accumulation of TAOH keeps trace of  $\cdot\text{OH}$  formation in the whole process. Total formed  $\cdot\text{OH}$  was 0.2-4.5  $\mu\text{mol L}^{-1}$ , which is comparable to that reported for aeration of anoxic groundwater (Page et al., 2013), even when taking into account some differences in the used reaction yields. No formation of TAOH was observed in blank experiments (TA added to Milli-Q water in the field and processed as for the other samples, and TA added to hypolimnion samples after full oxygenation).

The dark formation of  $\cdot\text{OH}$  upon aeration of anoxic water has been attributed to Fenton and Fenton-like processes (Page et al., 2012; Page et al., 2013). They could involve either Fe(II) (which could produce  $\text{H}_2\text{O}_2$  when undergoing oxidation to Fe(III), thereby triggering the Fenton reaction; Morgan and Lahav, 2007; Pignatello et al., 2006; Page et al., 2013) or hydroquinones/semiquinone radicals. The latter could induce Fe-free Fenton-like reactions (Klöpffel et al., 2014; Chen and Pignatello, 1997; Zhu et al., 2007), but organic and possibly inorganic reductants are also known to enhance the Fe-based Fenton process by favouring the Fe(III)-Fe(II) recycling (Georgi et al., 2007; Fukuchi et al., 2014; Murphy et al., 2014).

Total Fe is reported in Table 1 (it was in the range of approximately 0.001-0.1  $\text{mg L}^{-1}$ , and it was higher for the bottom samples), but its concentration did not match clearly the observed results. Fe levels could possibly account for the higher TAOH formation in the B2 sample of AV compared to B1 (total Fe was higher in B2 by over an order of magnitude), but the bottom samples richest in Fe were those from CA and SdS and they yielded the lowest formation of TAOH. A possible explanation is that the content and oxidation state of organic matter is as least as important as Fe in the process, due to the likely involvement of reduced organic compounds in Fe(III)-Fe(II) recycling and/or in Fe-free Fenton-like reactions. For lake SdS the  $\cdot\text{OH}$  formation could be limited by the low DOC values (little organic matter available, see Table 1), and in the case of CA the low water depth (7 m) might favour some  $\text{O}_2$  diffusion to the hypolimnion that, while below the detection limit of the used oxygen meter, could affect the oxidation state of organic matter. The bottom water in lakes AV and VI is deep enough to limit oxygen diffusion and it has a sufficient content of organic matter to produce an enhancement of Fenton reactions, which might account for the elevated formation levels of dark  $\cdot\text{OH}$ .

The complexity of the involved reactions places the elucidation of the  $\cdot\text{OH}$  production pathway(s) outside the scope of this short communication and it will be the topic of further investigations. The part that follows will discuss the potential environmental significance of the process.

To assess the importance of dark  $\cdot\text{OH}$  formation, one can compare dark production with photochemical  $\cdot\text{OH}$  generation in the sunlit epilimnion or with other photoinduced processes. Photochemical reactions were modelled with the APEX software. The comparison was initially carried out on a mole per litre basis, neglecting the issues related to the relative volumes of the hypolimnion and the epilimnion. Such issues will be discussed later.

Taking Lake AV (sample B2) as an example, APEX modelling showed that the production of 4.5  $\mu\text{mol L}^{-1}$  of total  $\cdot\text{OH}$  as in the dark process would require  $\sim 4$  months of epilimnion irradiation,

under clear-sky conditions in spring or summer (e.g. April to August). The cumulated irradiance would correspond to around 55% of the total sunlight input received yearly by the lake, and to even more when considering weather-related issues. In the case of sample B1, the corresponding data would be ~2 months of epilimnion irradiation and ~30% of the yearly sunlight input. In the other cases, the amount of dark  $\cdot\text{OH}$  produced by aerated anoxic water would be equivalent to almost 3 months epilimnion irradiation for VI, 1-3 days for CA, and 1-1.5 days for SdS. In two out of four cases (AV and VI), oxygenation of anoxic epilimnion water has the potential to play an important role in the  $\cdot\text{OH}$  budget of lake water.

By using APEX, one can also compare pollutant degradation by photochemical and dark processes in the AV and VI cases, for which the dark process may be important. A full set of photoreactivity parameters has recently been reported for the fungicide dimethomorph (DMM) (Avetta et al., 2014), which allows for the modelling of phototransformation kinetics based on water chemistry and depth. The photochemical DMM half-life time ( $t_{1/2}^{\text{DMM}}$ ) in the epilimnion would be ~1.5 months (in spring/summer) for both AV and VI, with an  $\cdot\text{OH}$  contribution to photodegradation of ~30% in both cases. The remaining phototransformation would be accounted for by reactions with the triplet states of organic matter and, to a limited extent (3-5%), by direct photolysis.

The DMM percentage that could be transformed by dark  $\cdot\text{OH}$  can be obtained by comparison between the dark and photochemical processes, by using the photochemical  $t_{1/2}^{\text{DMM}}$ , the role of  $\cdot\text{OH}$  in DMM transformation (from which one gets the first-order reaction rate constant of DMM transformation by  $\cdot\text{OH}$  alone,  $k^{\text{DMM}-\cdot\text{OH}}$ ) and the epilimnion irradiation time needed to produce the same total formed  $\cdot\text{OH}$  as in the dark. This approach holds under the hypothesis that natural water components (mostly organic and inorganic carbon) scavenge  $\cdot\text{OH}$  to the same extent in both dark and irradiated compartments. Table 1 shows that differences in the relevant parameters between epilimnion and hypolimnion water were not substantial for AV and VI, but water from the lake surface had higher pH than that in the bottom. This issue implies a higher concentration of carbonate in the epilimnion that could induce a more efficient scavenging of  $\cdot\text{OH}$  (Al Housari et al., 2010). Considering that oxygenation of anoxic hypolimnion water would imply some mixing, leading to intermediate chemical composition, here it is hypothesised for simplicity that the  $\cdot\text{OH}$  scavenging is the same for both the dark and the photochemical processes. This approximation might induce an underestimation of the importance of the dark process.

In the case of AV-B1, the total  $\cdot\text{OH}$  formed in the dark would be photochemically produced in ~4 months of epilimnion irradiation (in spring-summertime conditions). Taking into account that the DMM photochemical half-life time in AV epilimnion is  $t_{1/2}^{\text{DMM}} \sim 1.5$  months (by all processes) and that the  $\cdot\text{OH}$  contribution to photodegradation is ~30%, one gets  $k^{\text{DMM}-\cdot\text{OH}} = 4.6 \times 10^{-3} \text{ d}^{-1}$  for DMM transformation by  $\cdot\text{OH}$ . The  $\cdot\text{OH}$  degradation of DMM is described by equation (1), where  $C$  is the DMM concentration at time  $t$  and  $C_0$  the initial concentration:

$$\frac{C}{C_0} = \exp(-k^{DMM-\cdot OH} \times t) \quad (1)$$

Equation (1), for  $t = 4$  months = 120 d, predicts  $C/C_0 = 0.58$  or a DMM degradation of 42%. The dark process, which produces about the same  $\cdot OH$  as 4 months of epilimnion irradiation, would also induce ~42% degradation of DMM.

By considering all the relevant samples, one obtains that dark  $\cdot OH$  could induce the transformation of 24-42% dimethomorph for AV and ~34% for VI. Even when taking into account that oxygenation of anoxic water may take place only once a year during lake circulation, these data look quite interesting. They could be even more interesting in the case of polymictic lakes subjected to frequent cases of anoxia and overturn (Kangur et al., 2013).

Due to the link between oxygenation and overturn, the actual volumes of the epilimnion and hypolimnion should be taken into account. Indeed, if the hypolimnion volume is very small compared to the epilimnion, the processes induced by its oxygenation would be proportionally less important. Figure S4 (SM) reports the bathymetric data of AV and VI (Regione Piemonte, 2004). To estimate the extension of the hypolimnion, the figure highlights the portion of AV that is deeper than 15 m and the portion of VI that is deeper than 20 m (which is the limit of anoxic water, see above). The figure suggests that the extension of the hypolimnion would be very significant in the case of AV, but one should consider that the maximum lake depth is 26 m. Therefore, depending on the chosen position of the water column, the depth of the hypolimnion would be lower than, or at most comparable with, that of the epilimnion. In the case of VI, most of the lake would be deeper than 20 m (Figure S4) and, in the fraction that is deeper than 40 m (which amounts to almost half of the lake extension) the hypolimnion depth would be higher than that of the epilimnion. Therefore, in lake VI, the volume of the hypolimnion would be comparable to that of the epilimnion and overturn would produce the oxygenation of an important fraction of the lake volume.

An additional caveat is that our experiments brought anoxic water in contact with oxygen till complete saturation, while overturn would probably produce a more gradual oxygenation. Column oxygen data for AV and VI (Regione Piemonte, 2004) indicate that both lakes have anoxic deep water for several months and that overturn produces oxygen saturation levels of 40-70% in the water column (with ~100% at the surface). However, compared to our experiments, contact times would be much longer and reduced species such as Fe(II) would still undergo oxidation in the presence of relatively small amounts of oxygen that would buffer the redox conditions (Tratnyek et al., 2011). Moreover, Fe(II) oxidation by  $O_2$  under lake-water conditions would take place on a time scale that is much faster than lake circulation phenomena (Craig et al., 2009). Therefore, the dark  $\cdot OH$  production is not expected to be much different compared to our estimates.



## Conclusions

This paper shows that aeration of anoxic lake water, sampled from the hypolimnion during the summer stratification period, leads to the dark production of measurable amounts of  $\cdot\text{OH}$ . In two of the studied lake-water samples the dark  $\cdot\text{OH}$  generation was potentially very important: on a mole per litre basis, it could lead to a total formed  $\cdot\text{OH}$  that would require, to be reached in the epilimnion, irradiation for several months under fair-weather summertime conditions. In the same lakes (AV and VI) the dark  $\cdot\text{OH}$  could induce significant degradation of pollutants, even when taking into account that oxygenation might take place only once a year in late summer-early autumn. To overcome the limitations of the concentration-based approach, one should take into account the volumes of both the epilimnion and the hypolimnion. The latter would be non-negligible but smaller than the epilimnion volume in AV. In contrast, for VI the hypolimnion would account for an important fraction of the lake volume. The results of this study suggest that in relatively deep lakes, if bottom water becomes anoxic during summer stratification, overturn might potentially cause an  $\cdot\text{OH}$  production amounting to a considerable fraction of the year-long  $\cdot\text{OH}$  budget. The latter may have important implications for *e.g.* pollutant transformation. The pathways involved in  $\cdot\text{OH}$  production upon oxygenation of anoxic lake water will require further investigation.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://xxxxxxxxx>.

## References

Aarnos H, Ylostalo P, Vahatalo AV. Seasonal phototransformation of dissolved organic matter to ammonium, dissolved inorganic carbon, and labile substrates supporting bacterial biomass across the Baltic Sea. *J Geophys Res* 2012;117:G01004.

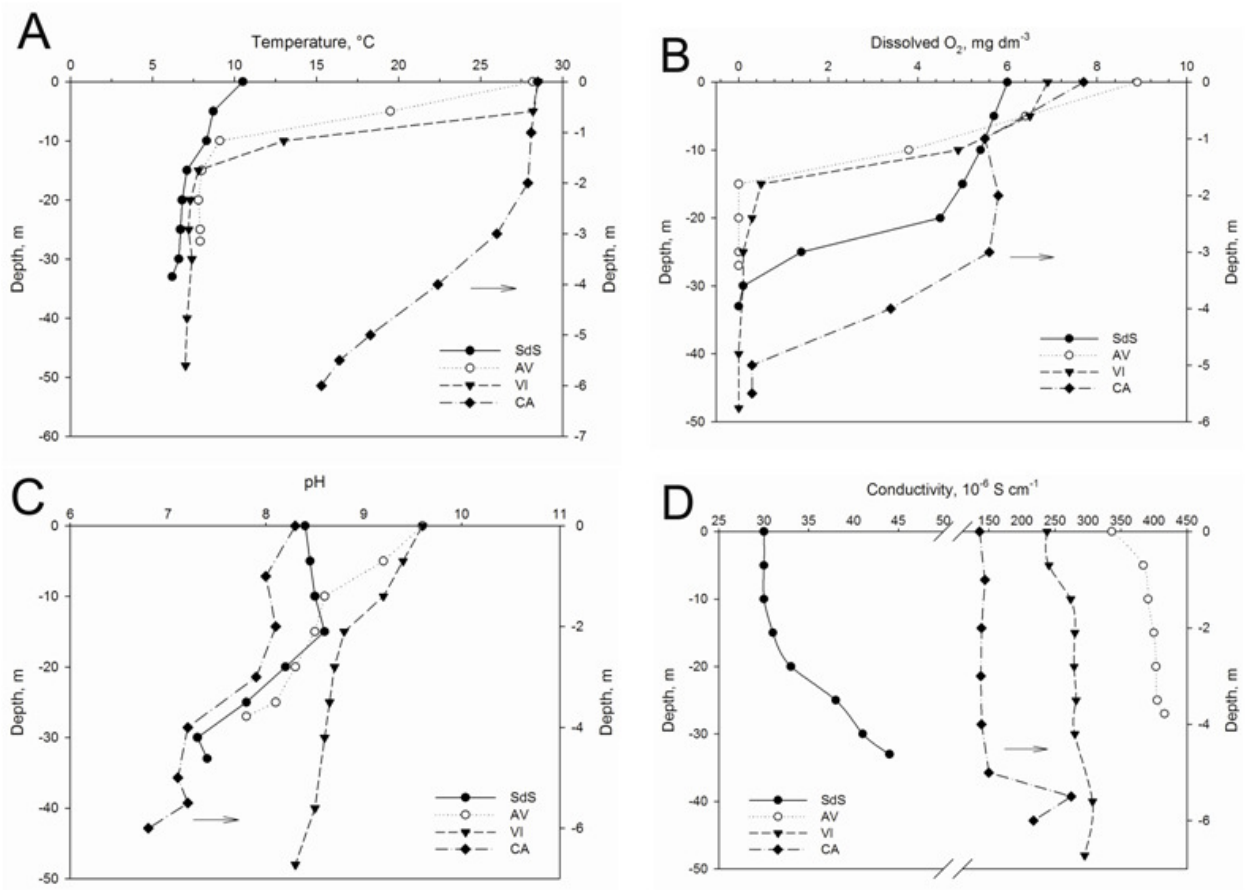
- Al Housari F, Vione D, Chiron S, Barbati S. Reactive photoinduced species in estuarine waters. Characterization of hydroxyl radical, singlet oxygen and dissolved organic matter triplet state in natural oxidation processes. *Photochem Photobiol Sci* 2010;9:78-86.
- Avetta P, Marchetti G, Minella M, Pazzi M, De Laurentis E, Maurino V, Minero C, Vione D. Phototransformation pathways of the fungicide dimethomorph ((E,Z) 4-[3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)-1-oxo-2-propenyl] morpholine), relevant to sunlit surface waters. *Sci Total Environ* 2014;500-501:351-60.
- Barbeau K, Rue EL, Bruland KW, Butler A. Photochemical cycling of iron in the surface ocean mediated by microbial iron(III)-binding ligands. *Nature* 2001;413:409-13.
- Bodrato M, Vione D. APEX (Aqueous Photochemistry of Environmentally occurring Xenobiotics): A free software tool to predict the kinetics of photochemical processes in surface waters. *Environ Sci Processes Impacts* 2014;16:732-40.
- Charbouillot T, Brigante M, Mailhot G, Maddigapu PR, Minero C, Vione, D. Performance and selectivity of the terephthalic acid probe for •OH as a function of temperature, pH and composition of atmospherically relevant aqueous media. *J Photochem Photobiol A-Chem* 2011;222:70-6.
- Chen RZ, Pignatello JJ. Role of quinone intermediates as electron shuttles in Fenton and photoassisted Fenton oxidations of aromatic compounds. *Environ Sci Technol* 1997;31:2399-406.
- Craig PS, Shaw TJ, Miller PL, Pellechia PJ, Ferry JL. Use of multiparametric techniques to quantify the effects of naturally occurring ligands on the kinetics of Fe(II) oxidation. *Environ Sci Technol* 2009;43:337-42.
- Fenner K, Canonica S, Wackett LP, Elsner M. Evaluating pesticide degradation in the environment: Blind spots and emerging opportunities. *Science* 2013;341:752-8.
- Fukuchi S, Nishimoto R, Fukushima M, Zhu QQ. Effects of reducing agents on the degradation of 2,4,6-tribromophenol in a heterogeneous Fenton-like system with an iron-loaded natural zeolite. *Appl Catal B: Environ* 2014;147:411-9.
- Georgi A, Schierz A, Trommler U, Horwitz CP, Collins TJ, Kopinke FD. Humic acid modified Fenton reagent for enhancement of the working pH range. *Appl Catal B: Environ* 2007;72:26-36.
- Kangur K, Kangur P, Ginter K, Orru K, Haldna M, Moels T, Kangur A. Long-term effects of extreme weather events and eutrophication on the fish community of shallow lake Peipsi (Estonia/Russia). *J Limnol* 2013;72:376-87.
- Klüpfel L, Piepenbrock A, Kappler A, Sander M. Humic substances as fully regenerable electron acceptors in recurrently anoxic environments. *Nat Geosci* 2014;7:195-200.
- Morgan B, Lahav O. The effect of pH on the kinetics of spontaneous Fe(II) oxidation by O<sub>2</sub> in aqueous solution – basic principles and a simple heuristic description. *Chemosphere* 2007;68:2080-4.

- Murphy SA, Solomon BM, Meng S, Copeland JM, Shaw TJ, Ferry JL. Geochemical production of reactive oxygen species from biogeochemically reduced Fe. *Environ Sci Technol* 2014;48:3815-21.
- Page SE, Sander M, Arnold WA, McNeill K. Hydroxyl radical formation upon oxidation of reduced humic acids by oxygen in the dark. *Environ Sci Technol* 2012;46:1590-7.
- Page SE, Kling GW, Sander M, Harrold KH, Logan JR, McNeill K, Cory RM. Dark formation of hydroxyl radical in Arctic soil and surface waters. *Environ Sci Technol* 2013;47:12860-7.
- Pignatello JJ, Oliveros E, MacKay A. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. *Crit Rev Environ Sci Technol* 2006;36:1-84.
- Posch T, Koester O, Salcher MM, Pernthaler J. Harmful filamentous cyanobacteria favoured by reduced water turnover with lake warming. *Nat Clim Change* 2012;2:809-13.
- Regione Piemonte. Water protection plan: Analysis of the impact of anthropic activities (in Italian). Technical attachment, Torino, 2004, 184 pp.
- Remucal CK. The role of indirect photochemical degradation in the environmental fate of pesticides: A review. *Environ Sci Processes Impacts* 2014;16:628-53.
- Tratnyek PG, Grundl TJ, Haderlein SB (eds.). *Aquatic Redox Chemistry*. American Chemical Society Symposium Series, Volume 1071, 2011.
- Wetzel RG. *Limnology: Lake and River Ecosystems*. 3<sup>rd</sup> ed., Academic Press, 2001.
- Zhu BZ, Kalyanaraman B, Jiang GB. Molecular mechanism for metal-independent production of hydroxyl radicals by hydrogen peroxide and halogenated quinones. *Proc Natl Acad Sci USA* 2007;104:17575-8.

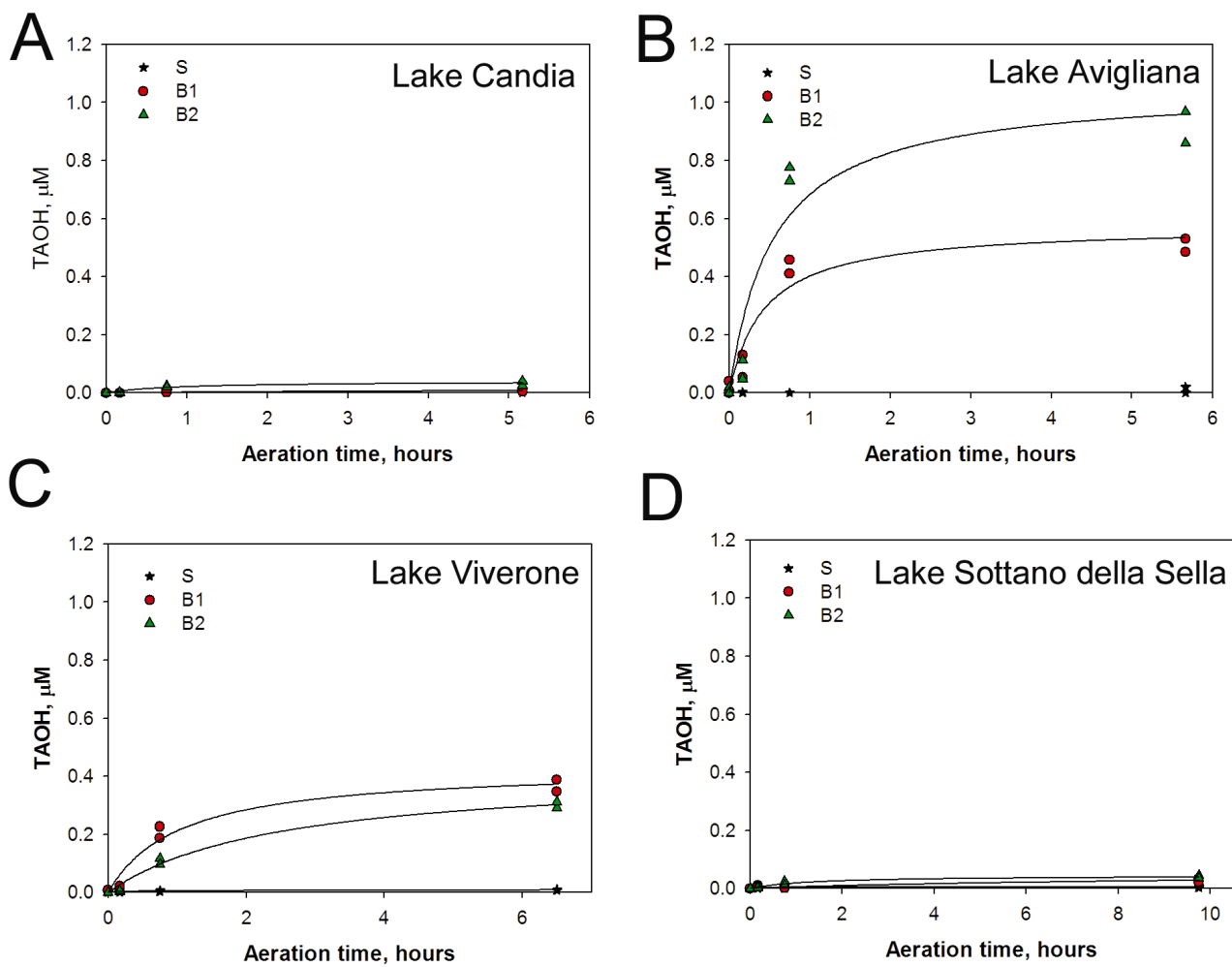
**Table 1.** Lake features <sup>(a,b)</sup> and chemical parameters (LOD = Limit of Detection; Surf = surface sample; B1-B2 = near-bottom samples; TC = total carbon; IC = inorganic carbon; DOC = dissolved organic carbon; TN = total nitrogen, Fe<sub>TOT</sub> = total iron).

	Surface Km <sup>2</sup>	Altitude m a.s.l	Max Depth m	Date of Sampling	NH <sub>4</sub> <sup>+</sup> (c) mg L <sup>-1</sup>	NO <sub>3</sub> <sup>-</sup> (c) mg L <sup>-1</sup>	PO <sub>4</sub> <sup>3-</sup> (c) mg L <sup>-1</sup>	TC mg C L <sup>-1</sup>	IC mg C L <sup>-1</sup>	DOC mg C L <sup>-1</sup>	TN mg N L <sup>-1</sup>	pH	Fe <sub>TOT</sub> µg L <sup>-1</sup>
<b>CA</b>	1.52	226	-7	10 Jul 2013									
<b>CA Surf</b>					0.065	0.015	< LOD (c)	18.66 ± 0.60	11.76 ± 0.42	6.90 ± 1.01	0.69 ± 0.11	8.3	2.4 ± 0.3
<b>CA B1</b>					2.48	0.001	< LOD (c)	23.86 ± 0.82	16.46 ± 0.25	7.40 ± 1.07	2.04 ± 0.12	7.2	43.7 ± 0.4
<b>CA B2</b>					3.18	0.016	0.033	23.17 ± 0.34	17.36 ± 0.17	5.81 ± 0.50	2.68 ± 0.10	6.8	101.8 ± 3.3
<b>AV</b>	11.5	352	-26	25 Jul 2013									
<b>AV Surf</b>					< LOD (d)	1.73	< LOD (e)	37.76 ± 1.08	31.95 ± 0.43	5.81 ± 1.51	0.78 ± 0.11	9.6	1.6 ± 0.4
<b>AV B1</b>					0.866	2.69	0.136	48.70 ± 1.39	43.53 ± 0.15	5.17 ± 1.54	1.72 ± 0.14	9.0	1.37 ± 0.1
<b>AV B2</b>					2.69	2.57	0.203	51.16 ± 1.33	45.59 ± 0.34	5.57 ± 1.67	2.96 ± 0.15	8.1	32.9 ± 0.8
<b>VI</b>	25.7	230	-58	30 Jul 2013									
<b>VI Surf</b>					0.152	0.001	< LOD (e)	26.59 ± 0.94	21.07 ± 0.37	5.52 ± 1.32	0.70 ± 0.10	9.6	0.61 ± 0.07
<b>VI B1</b>					1.44	0.052	1.165	33.75 ± 0.90	29.08 ± 0.23	4.67 ± 1.12	1.39 ± 0.14	8.3	15.7 ± 0.2)
<b>VI B2</b>					0.690	0.018	0.865	32.35 ± 1.41	27.66 ± 0.62	4.69 ± 2.03	1.00 ± 0.08	8.5	7.7 ± 0.4
<b>SdS</b>	1.1·10 <sup>-4</sup>	1862	-33	22 Jul 2013									
<b>SdS Surf</b>					0.091	0.889	< LOD (c)	2.26 ± 0.06	1.67 ± 0.00	0.59 ± 0.06	0.34 ± 0.09	8.4	< LOD (c)
<b>SdS B1</b>					0.963	1.05	< LOD (c)	3.28 ± 0.12	2.92 ± 0.06	0.35 ± 0.18	0.45 ± 0.09	8.1	56.4 ± 0.4)
<b>SdS B2</b>					0.466	1.00	< LOD (c)	2.68 ± 0.07	2.49 ± 0.06	0.19 ± 0.12	0.39 ± 0.09	7.4	17.4 ± 0.2)

(a) [www.regione.piemonte.it](http://www.regione.piemonte.it); (b) [www.parks.it/parco.lago.candia](http://www.parks.it/parco.lago.candia); (c) The reproducibility of repeated runs for cations and anions was 4-5%; (d) LOD = 0.018 mg L<sup>-1</sup>; (e) LOD = 0.01 mg L<sup>-1</sup>.



**Figure 1.** Temperature (A), dissolved oxygen (B), pH (C) and conductivity (D), as a function of the lake depth. SdS: Lake Sottano della Sella; AV: Lake Avigliana; VI: Lake Viverone; CA: Lake Candia. Note that depth for CA is always reported on the right Y-axis.



**Figure 2.** Time trend of TAOH formed from 1 mM TA in hypolimnion and surface samples exposed to the atmosphere. (A) Lake Candia; (B) Lake Avigliana; (C) Lake Viverone and (D) Lake Sottano della Sella. The curves on the plot are just guides for the eye.