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Degassing Pit Lakes: Technical Issues and Lessons Learnt from the HERCO$_2$ Project in the Guadiana Open Pit (Herrerías Mine, SW Spain)

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Abstract

The unique case of carbon dioxide accumulation in the bottom layer of the acidic lake formed in the Guadiana open pit (Herrerías mine, SW Spain) led to exceptionally high dissolved gas pressures (ca. 5.0 bar at depths of 50-70 m). This CO$_2$ has formed by carbonate (calcite, dolomite) dissolution during decades of interaction of the acidic water with the pit wall rocks. The elevated dissolved gas pressures were only comparable to those found in the volcanic crater lakes of Cameroon like Nyos and Monoun, which erupted in the 1980s and sadly triggered the loss of hundreds of human lives. This gas pressure was not far from the absolute (hydrostatic plus atmospheric) pressure limiting CO$_2$ solubility at depth, thus making this pit lake potentially dangerous for the possibility of a hypothetical limnic eruption. Following detailed field and experimental studies aimed at deciphering the source and accumulation patterns of CO$_2$ in the lake, a degassing project started in 2014, which followed an upscaling strategy with construction and installation of progressively bigger pipelines capable of extracting increasingly higher flow rates of CO$_2$-charged water from the deep part of the lake. As of May 2019, the degassing systems have successfully extracted most of the CO$_2$ originally present in the lake (i.e. ≈ 123,000 m^3 CO$_2$), which has been discharged to the atmosphere in a controlled and safe way. The fountains became progressively smaller and finally stopped, due to the decreased gas pressure at depth. The larger pipes will serve as a regulating system in the future. This paper describes the main findings encountered during the degassing project, some relevant technical issues observed during the last five years (2014-2019), and lessons learnt from the Guadiana pit lake experience.

Keywords Acidic mine pit lakes, Dissolved carbon dioxide, Limnic eruption, Controlled degassing

Introduction

The discharge of untreated or poorly treated acid mine drainage (AMD) commonly causes environmental problems in nearby streams, lakes, reservoirs, aquifers, and soils, and strongly limits the usability of water resources (e.g. Geller et al 2013; Nordstrom and Alpers 1999; Younger et al. 2002, and references therein). AMD has also been directly linked to health risks for local inhabitants (e.g. As contamination of groundwater or surface water). In the particular case of pit lakes, the combination of geochemical processes typical of AMD systems with physical features characteristic of lakes make them potentially hazardous for a number of reasons. The most obvious is the accumulation of reduced and potentially harmful gases like H$_2$S, CH$_4$, or NH$_3$, due to microbial activity at depth (e.g., Boehrer et al. 2017). Many pit lakes tend to be meromictic (permanently stratified) due to their high relative depth (Schultze et al. 2017), so these gasses can accumulate for decades. The concern is that an eventual turnover could release these gases, causing chemical changes in surface water, with effects that would largely depend on environmental conditions and the use given to that particular pit lake (e.g. recreation, fishing, water supply).

Of particular concern, due to its potentially destructive capacity, is the hypothetical accumulation of large amounts of carbon dioxide (CO$_2$) in the deep part of these lakes. In a mine water-related conference held in 1997, WM Murphy was the first to raise the question of whether pit lakes could be susceptible to limnic eruptions like the so-called "killer" volcanic lakes Nyos and Monoun in Cameroon (e.g. Halbwachs et al. 2004; Kling et al. 1994, 2005; Tanyleke et al. 2019). Seventeen years later, a paper by Sánchez-España et al. (2014) documented, for the first time, the accumulation of very high levels of CO$_2$ in the deep part of an acidic pit lake in SW Spain. This CO$_2$ was seen to be chiefly due to the dissolution of carbonates (mainly calcite and dolomite) present in volcanic (basaltic) rocks in the mine site by the acidic water. Two years later, another paper by Boehrer et al. (2016) reported the successful performance of pilot-scale degassing pipes installed in the pit lake, and quantified more precisely the concentration of different gases (CO$_2$, N$_2$, CH$_4$) and the resulting total dissolved gas pressure. The publication of this second paper, however, had a great impact on national and international media (e.g. Ansede 2016), and provoked unjustified alarm among locals and regional authorities (Sánchez-España et al. 2018).

An agreement was signed between the Spanish Geological Survey (IGME) and the mining authorities of the Andalusian Government (Bureau of Mines, Division of Industry, Energy and Mining), with other research institutions (Helmholtz Centre for Environmental Research-UFZ, University of the Basque Country) participating, to start a degassing project to eliminate the possibility of a potentially dangerous gas outburst. This project, based on the encouraging results of pilot-scale trials, included the installation of large, permanent pipes in the pit lake and continuous monitoring of the dissolved gas pressure at depth. The HERCO$_2$ project started in September 2017 with the installation of the first pipe; a second pipe was installed in October 2018. The two pipes operated until March (Pipe 1) and May (Pipe 2) 2019, and successfully evacuated most of the CO$_2$ that had accumulated in this pit lake for decades. The design of these degassing pipes was inspired by technology developed and successfully applied in lakes Nyos and Monoun during the last 15 years (Halbwachs et al. 2004; Kling et al. 2005; Tanyleke et al. 2019).

In this paper, we report the main activities carried out during this project, as well as the most relevant findings, difficulties, peculiarities, and technical problems encountered during the course of the degassing operations. Our main goal is to share our experience with researchers, technicians, managers, institutions, and companies with current interest and activity in flooded pits, so that what we have learned can be used if a similar case occurs in the future. In addition, it is our aim to highlight the importance of geochemical and limnological research and monitoring programs in abandoned flooded mine sites to avoid or minimize safety and health risks.

Site Description and Environmental Framework

The open pit of the Guadiana mine is part of a larger mine complex called Minas de Herrerías, in the province of Huelva (SW Spain) (Fig. 1). This complex included two open pits (Guadiana and Santa Bárbara) and two big shafts, which connected with the Guadiana pit by a framework of sub-horizontal mine galleries (Pinedo Vara 1962). The deeper galleries lie at a depth of 220 m below the topographic surface. The Guadiana mine was active from 1895 to 1990, and involved both underground and open pit mining. The orebody consisted of dominant pyrite with minor accompanying sphalerite, chalcopyrite, galena, and arsenopyrite.

Figure 1 will be placed near here during the printing process

This whole area surrounding the pits is covered by tailings and waste piles, and includes several dams of acidic, metal-rich water (Fig 1). The Guadiana open pit started flooding around 1995, a few years after its abandonment. The resulting pit lake has been increasing in volume since then, and today presents a surface area of ≈ 20,000 m^2 and a maximum depth of 70 m in its central zone. The neighbouring Santa Bárbara pit lake is not connected with Guadiana, and presents a very different colour due to its much shallower depth (15 m) and very different composition (pH 4.7, with no dissolved ferric iron; López-Pamo et al. 2009).

The pit lake is now part of a mining aquifer that also includes a system of flooded galleries and shafts connected to the pit and the surrounding rock framework formed by altered and highly fractured volcanic rocks. The increased water level in recent years suggests that the pit is still being recharged by groundwater at depth, very likely through conduits, such as the main tunnels. From a hydrogeological perspective, the mine system seems to behave similar to karstic systems, with relatively fast circulation of water by such conduits and rock dissolution, which includes disseminated carbonates in several lithologies.

Methods

Depth profiling of physico-chemical parameters has been carried out every 3-5 months with a MS5 multi-parametric probe from Hydrolab (Hach) operated from a rubber boat. All sensors were carefully calibrated on site with appropriate standards. The total dissolved gas (TDG) pressure was mostly measured with a Hach TDG sensor. This sensor consists of a transducer connected to a helical gas-permeable membrane. The sensor needs around 20 min to stabilize, which is roughly the time required to allow equilibrium of dissolved gas pressure on both sides of the membrane. Because of this long stabilization time, TDG measurements were usually conducted at selected reference depths (e.g. every 5-10 m). The measuring range of this sensor is 0-2100 mm Hg (0-2.76 bar). Because the TDG pressure in the deep part of Guadiana pit lake far exceeded the upper range limit, the TDG pressure had to be measured by other methods, including gas sampling with specific gas-tight sampling bags (TecoBAG, Tesseraux, Germany) connected to a submersible pump (2013-2016; see Boehrer et al. 2016 or Horn et al. 2017 for a detailed explanation of the method; Fig. 2c), and direct TDG measurement with a custom made probe (Pro Oceanus, Bridgewater, Canada) able to measure gas pressures up to 18 bar and depths up to 500 m.

Figure 2 will be placed near here during the printing process

Water samples were also regularly collected at selected depths to follow the chemical evolution of the lake during the degassing operations. These water samples were taken with a Van Dorn limnologic bottle with 5 L volume (Fig. 2), immediately filtered (0.45 µm) and acidified (HCl 1 M) on site, and preserved at 4 º C during transport to the lab.

Ion concentrations in water samples were analyzed by atomic absorption spectrometry (AAS) and by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using Varian SpectrAA 220 FS and Agilent 7500ce instruments, respectively. The analytical detection limits were usually below 1 µg/L for most trace elements.

Results and Discussion

Preliminary Research and First Degassing Prototypes

Table 1 provides a brief review of some relevant milestones and important dates concerning research and initiatives conducted in the Guadiana pit lake during the last decade. In the first visits and preliminary investigations conducted between 2008 and 2010, several observations suggested the presence of an extreme concentration of dissolved gas in the deep part of the pit. First, the sampling bottle reached the boat with a very high pressure and intensely sparkling water, which often provoked the opening of regulating valves (Fig. 2b). Second, sediment cores taken from the bottom appeared totally mixed and homogenized due to degassing during the uplift. Third, bathymetric surveys with double-beam ecosounders gave inaccurate readings in the deepest part of the lake, such as apparent depths of 40 m at zones where the depth had been manually measured at ≈ 60 m. Physico-chemical profiles indicated the absence of gases like O_2 or H_2S, even at trace amounts. The CO_2 content was measured by spectrophotometry, which gave maximum concentrations exceeding 3200 mg/L CO_2 at depths of 45 m. However, no reliable measurements could be made in the deeper part due to intense degassing during sample handling (Sánchez-España et al. 2014). The first precise measurement of CO_2 concentration and resulting gas pressure for this part was conducted in December 2013 with the help of gas-tight sampling bags followed by gas volume measurement and chemical analyses by gas chromatography (Sánchez-España et al. 2014; Fig. 2c-d). The obtained values ($[CO_2]$=5000 mg/L, pCO_2=3.6 bar) strongly recommended more careful investigations and the implementation of some correcting measure to reduce any safety risk in the area. The major threat considered at that moment was that some external factor (e.g. a landslide or small-scale earthquake) could trigger a limnic eruption. To test the feasibility of extracting the gas-charged water from the deep part of the lake by degassing pipes, two different pilot-scale pipes were installed in 2014 (Boehrer et al. 2016; Table 1; Fig. 2e-h). These trials worked successfully for two (prototype 1) to four (prototype 2) years.

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The flow rates of these trials, however, were very low, with discharge rates between 2 L/min (prototype 1) and 10 L/min (prototype 2). A simple calculation using those flow rates and the estimated volume of gas-charged deep water to be evacuated (around 114,000 m^3, considering only depths below 45 m, where gas pressures increased dramatically; Boehrer et al. 2016) indicated a required degassing time of ≈ 18 years. This obviously indicated an urgent need to upscaling the project by installing a larger pipe, which could provide much higher flow rates and reduce the duration of the degassing operations. A new project was started in 2017 under contract with the Bureau of Mines of the Andalusian Government (Table 1; Figs. 3-4).

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Installation of Permanent Degassing Pipes and Associated Protective Measures

A new pipe (Pipe 1) installed in September 2017 with a PVC hose (10 atm) of 50 mm diameter and 61 m in length yielded a 3 m high fountain with flow rate of 50 L/min (Fig. 4c). Along with the second prototype, which was still active at that time, this gave a total discharge of 60 L/min (Fig. 3a). Although this was a five-fold flow augmentation relative to the previous pipes, the evolution of gas pressures at depth was not as fast as expected For this reason, an additional, larger pipe (Pipe 2, 63 mm diameter and 65.5 m in length) was installed in June 2017 (Fig. 3b).

This new pipe could not be activated at first, since conventional motor pumps could not provide stable flow rates and no fountain formed during pumping (Fig. 3c). Subsequent trials in October 2018, with membrane pumps (much more appropriate for pump gas-rich water) could activate this second pipe, which created a fountain 3.5 m high and yielded a discharge of 60 L/min. The total discharge of both pipes amounted to ≈ 90 L/min (Fig. 4), ensuring lake degassing could proceed in a reasonable time period. However, both pipes included reductions at the discharge points, which helped improve sparkling but also reduced the flow rate. Thus, a month later, these reductions were removed to increase the flow rate, and the combined discharge increased again, to 113 L/min. The main features of all of these pipes during 2014-2018 are summarized in Table 2 and illustrated in Fig. 4.

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Coinciding with the installation of these new pipes, some other works were also accomplished, including inspection of fractures and deteriorated platforms in the pit (Fig. 3f), collection and investigation of drill core remnants from the mine site to assess local geology and mineralogy (Fig. 3g), and installation of warning signboards (Fig. 3h-i).

Overall Performance of the Degassing Pipes

Fig. 5 illustrates the effects of the degassing on dissolved gas pressure in the pit lake during the last five years. TDG profiles taken in different periods from December 2013 to May 2019 with the Hach membrane sensor (hence limited by the 2.7 bar sensor limit) are displayed in Fig. 5a, while those obtained by the gas-sampling method or by the custom-made probe are given in Fig. 5b. In the latter, the horizontal scale has been enlarged to display the absolute pressure as a reference.

Figure 5 will be placed near here during the printing process

In both plots, the temporal evolution of TDG clearly shows a continuous decrease of dissolved gas pressure due to degassing. Although the decrease in TDG has occurred in the whole water column below 20 m, the drop in gas pressure has been especially important at depths below 50 m (Fig. 5 and Fig. 6a). This point is particularly important, as it has decreased gas pressures in the deep water from close to 5 bars in 2013, which was not too far from the absolute pressure (hydrostatic plus atmospheric) limiting gas solubility, to values of 1.0-1.8 bars at present, which can be considered safe (Fig. 5b).

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The continual decrease of the fountains' heights and flow rates provide indirect evidence of this drop of dissolved gas pressure at depth during the degassing period. As an example, Pipe 1 started working in September 2017 with a fountain height of 3 m and a flow rate of 50 L/min; then it gradually decreased over the next 17 months of operation (e.g. 1.5 m and 30 L/s in November 2018; Fig. 4c-e) until it finally stopped in February 2019. This was due to the decreasing gas pressure at the extraction depth (60-61 m), which delivered the driving force of the ascending vertical flow of gas-charged water through the pipe.

Considering the respective flow rates and times of operation of the four pipes between October 2014 and May 2019, the total amount of gas-charged deep water pumped to the surface has been estimated at ≈ 74,000 m^3. This calculation accounts for the progressive decrease in flow rate (based on observations during systematic visits) of all pipes. This volume of water roughly corresponds to the volume of water between depths of 45 m (the depth at which TDG pressure increased exponentially in 2013) and 60-61 m (suction depths of the prototypes and Pipe 1), ≈ 80,000 m^3. Based on this calculation, it can be assumed that most of the CO_2-rich deep water has already been evacuated to the surface and released most of the dissolved CO_2 to the open atmosphere in a gradual and safe way.

The total amount of CO_2 released to the atmosphere during this period would approach 123,000 m^3 (Fig. 6b). This calculation has already considered the respective concentrations and pressures measured in the deep water and their variation with time, as well as the resulting theoretical volumes at the surface (1 bar). This approximation exceeds that initially estimated in a previous paper (80,000 m^3 of pure CO_2 accumulated below depths of 45 m; Boehrer et al. 2016). However, the previous estimation was based on depth profiles conducted in 2013 and 2014, when the pit lake had a surface area of 18,000 m^2, a maximum depth of 65 m, and a volume of ≈ 590,000 m^3. In contrast, due to the continuous input of groundwater recharge from adjacent mine galleries and the mine aquifer, the pit lake now has a surface area of ≈ 20,000 m^2, a maximum depth of 70 m, and a volume of ≈ 690,000 m^3. Therefore, it can be concluded that the degassing pipes have been extracting CO_2 not only from the deep water originally contained in the pit lake at the time of the first studies, but also from nearby groundwater feeding the pit lake, which very likely also contains large amounts of CO_2. If abruptly released to the atmosphere in a hypothetical eruption, this amount of CO_2 could have formed a potentially lethal cloud of pure CO_2 ≈ 6 m thick immediately above the pit lake surface. The stability and physical behaviour of this hypothetical cloud would have been strongly dependent on physical processes such as diffusive or convective transport, wind currents, air temperature, etc. The high vertical walls existing in the pit above the lake surface would have probably favoured the retention of the CO_2 cloud within the pit, though the consequences of this gas outburst would have been largely unpredictable.

Fig. 6b clearly show that the rate of degassing greatly increased with the installation of the Pipe 1, and again with the installation of Pipe 2. Thus, Pipe 1 was able to extract 60,000 m^3 CO_2 in only 500 days, and 28,000 m^3 CO_2 were extracted between Pipe 1 and Pipe 2 in 260 days, while the two prototype pipes removed 40,000 m^3 in 1000 days (Fig. 6b). Together, these pipes accomplished the objectives raised by the authorities and have made the pit lake relatively safe, as far as gas pressure is concerned.

Effects of Degassing on Pit Lake Stratification

The effects of the degassing actuation on pit lake stratification can be observed in the vertical profiles of Fig. 7, which show the temporal evolution of temperature, specific conductance, pH, and oxidation-reduction potential (ORP). All these plots reveal that the continuous self-sustained pumping of deep water to the surface has gradually thickened the mixolimnion and deepened the chemocline, which moved from a depth of 10 m in October 2014 to 41 m at present (Fig. 7a-d). The chemical modifications of the pit lake during the degassing period have been really important, as expected from the extremely high concentrations of dissolved sulphate, ferrous iron, and many other metals (Zn, Mn, Mg, Co, Ni, etc.) contained in the deep water, which far exceeded those of the surface (Sánchez-España et al., 2014). The whole mixolimnion has experienced a gradual acidification (from ≈ pH 3.0 in 2014 to pH values between 2.0 and 2.5 at present; Fig. 7c) due to the continuous oxidation of Fe(II) and subsequent precipitation of Fe(III), mostly as schwertmannite with a minor amount of jarosite (Sánchez-España et al. 2016).

Figure 7 will be placed near here during the printing process

In the same way, dissolved solids (as indicated by specific conductance) also continuously increased at the lake surface (4600 µS/cm in 2014 vs. 7400 µS/cm in 2019; Fig. 7b), and ORP has evolved in certain layers (between depths of 30 and 50 m) from 50 mV in 2014 to 400-550 mV in 2019 (Fig. 7c). The physico-chemical changes at depth have also been drastic; for example, water temperatures between 40 and 60 m have decreased by up to 9 º C (Fig. 7a) and specific conductance has dropped by 25-30% to even 50% at 40 m (Fig. 7b).

Furthermore, self-sustained degassing through the pipes has continuously removed water from the deepest layer, moving shallower waters of lower density progressively to greater depths. As a final result, the thickness of the CO_2-rich bottom layer shrank from 25 m in 2014 to 4-5 m above the pit lake bottom at present (Fig. 8a-d).

Figure 8 will be placed near here during the printing process

In the schematic representation given in Fig. 8(a-d), we have not included the rest of the “mining aquifer” composed of galleries and shafts connected to the pit (Fig. 8e). However, it is evident from the aforementioned observations that CO_2 production is not restricted to carbonate dissolution in the pit walls, but also occurs in the rest of the mine complex and wherever carbonate minerals exist in contact with acidic water. Thus, a portion of the CO_2-rich water extracted from the deep part of the lake would actually correspond to groundwater entering the pit lake from some of the tunnels (Fig. 8e). In this sense, some uncertainty exists about the possible evolution of gas pressures at depth in this mine site now that the current gas pressure is not sufficient to sustain stable vertical ascending flow along the pipes.

Effects of Deep-water Degassing on Pit Lake Chemistry

Pumping deep water to the lake surface has impacted water quality negatively, especially regarding the upper part of the lake. This deterioration became evident soon after degassing activities began (Fig. 9). The pit lake changed colour from greenish to deep red in a few months, due to fast Fe(II) oxidation and massive schwertmannite precipitation (Fig. 9a-b). The upper part of the pipes was also densely covered by thick mineral coatings containing a mixture of schwertmannite, jarosite, goethite, hydrobasaluminite (resulting from Al precipitation), and gypsum (Fig. 9c-d). The present aspect of the pit lake denotes the current concentration of dissolved ferric iron (350 mg/L Fe[III]) and the abundance of ferric colloids in the lake surface (Fig. 9e).

Figure 9 will be placed near here during the printing process

The chemical effects of deep water pumping are also reflected in the evolution of dissolved oxygen in the upper part of the lake (Fig. 10a), which has evolved from concentrations of 7-8 mg/L O_2, representing ≈ 100% saturation at its corresponding temperature (usually, 13-25 º C; Fig. 7a) to very low or negligible, depending on the depth considered. This marked drop has resulted from the high chemical oxygen demand of dissolved ferrous iron oxidation, which takes place at the lake surface once the reduced deep water has discharged and mixed in the mixolimnion.

The vertical profiles for metals like Fe, Zn, and Mn (Fig. 10b-d) also illustrate this contrasting evolution between the upper mixolimnion, where metal concentrations have increased significantly due to the introduction of metal-rich deep water to the surface and the deep monimolimnion, where metal concentrations have progressively decreased. Metal increase in the mixolimnion was also evident in the suspended particulate matter retained in filters, which was denser and showed a reddish colour with increased Fe and S content (*not shown*).

Figure 10 will be placed near here during the printing process

Technical Issues Regarding TDG measurement

An evident conclusion concerning total gas pressure measurements (see Fig. 5a) is that the Hach TDG sensor was designed to survey fish ponds and water treatment plants, but not extremely gas-charged water bodies like the Guadiana pit lake. It required a major effort to convince a manufacturer to build a total pressure sensor for much higher gas pressures and a much greater deployment depth. We appreciate the generous support by Pro Oceanus in providing a total gas pressure sensor Mini-TDG with a shorter response time for the conditions in Lake Kivu (Boehrer et al. 2019). This sensor was also used for direct gas pressure measurements in the Guadiana pit lake in 2017 (see Fig. 11a).

Figure 11 will be placed near here during the printing process

Given the very long stabilization time of the Hach TDG sensor, a different approach had to be used sometimes. This approach consisted of limiting the measuring time at each point to 20 min (as indicated by the company), and then plotting the data set to extrapolate the data until they asymptotically approached certain values (Fig. 11b).

Dissolved Gas Pressure Monitoring in Other Pit Lakes as a Predictive Tool

Considering the alarm generated by Guadiana pit lake, we decided to investigate some other pit lakes in the area and in other mining districts to check if a similar situation could be found in other flooded pits. We initially selected pit lakes that met the requisites needed to accumulate CO_2 at depth, namely: (1) high depth-to-surface ratio ensuring meromixis and thus avoiding lake turnover, (2) local geology containing carbonates susceptible to acid dissolution, (3) low pH values (i.e. below 4-5) forcing all dissolved inorganic carbon to be present as CO_2 (i.e. without any bicarbonate or carbonate ions), and (4) long time period after mine closure and flooding, so that CO_2 could have accumulatied for some decades. The TDG profiles obtained in some of these pit lakes (e.g. La Zarza and Filón Centro in the Iberian Pyrite Belt in SW Spain, or Brunita in the La Unión mine district in SE Spain) and some others taken in previously studied pit lakes (e.g. Cueva de la Mora or San Telmo; Sánchez-España et al. 2013; Schultze et al. 2017) are displayed in Fig. 12.

Figure 12 will be placed near here during the printing process

As can be deduced from the TDG profiles of Fig. 12, the Guadiana pit lake case seems to be quite unique. None of the other pit lakes has developed even a remotely similar situation with regard to elevated dissolved CO_2 pressures. Only Cueva de la Mora, which displayed peak TDG values of 2.3 bar near the pit lake bottom at depths of 35- 40 m (Fig. 12). The acidic pit lake of Brunita, in the La Unión mining district, has developed TDG pressures of ≈ 1.5 bar above the sediments at 22 m depth, resulting mostly from carbonate (siderite, dolomite) dissolution and the consequent release of CO_2. Most other pit lakes (La Zarza, Filón Centro, San Telmo) showed low TDG values at depth, which were all very far from the absolute value, and apparently do not represent a safety risk at this moment. It would be advisable, however, to follow the temporal evolution of TDG values and CO_2 concentration in pit lakes like Cueva de la Mora or Brunita, since such data would allow rates of CO_2 accumulation to be calculated in these mine sites and predict possibly dangerous scenarios in the future.

General Conclusions and Lessons Learnt

Below we provide some recommendations and considerations arising from the HERCO$_2$ project in the Guadiana pit lake with respect to safety, mine water-related research, and other technical issues.

Civil Responsibilities in Abandoned Flooded Pits

An evident conclusion from the Guadiana pit lake case is that leaving flooded mine sites unattended and without any kind of vigilance by well-trained technicians is not an advisable practice. Modern mining companies are at present legally obligated to take care of safety and environmental issues related with mine water after mine closure and reclamation. There are many examples in Spain and worldwide where currently flooding pits have been subject to intensive monitoring programs and scientific research. Spanish examples include the Meirama coal mine pit lake in Galicia (Delgado et al. 2013), Reocín Pb-Zn mine pit lake in Cantabria (López-Pamo et al. 2010), and the Aznalcóllar mine pit lake in Seville (Santofimia et al. 2007; Schultze et al. 2006). All these examples represent a successful collaboration between mining companies, environmental or regulatory agencies, and research institutions. However, this was not the case in the past: most open pits were abandoned, without any kind of environmental control. With the mining companies usually dissolved and disengaged of any civil responsibility, the corresponding mining authorities have been in charge of maintaining a minimum degree of safety at these abandoned mine sites. Initiatives by these authorities, however, have been usually limited to building protective fences around the pit lakes to avoid accidents, and to place warning signs. Hydrogeological surveys or geotechnical studies have been completely non-existent in these flooded mine pits, and the general state of many of them is rather poor with regard to structural stability of slopes. Most of the research conducted in these pit lakes has been accomplished by government agencies and research institutes through research projects, demonstration projects, or PhD theses. It would be highly advisable that the mining authorities with civil responsibility in these abandoned mine areas would run their own controls and monitoring programs with the aim of reducing the possibility of dangerous events.

Future Evolution of Guadiana Pit Lake

The future evolution of Guadiana pit lake is uncertain. Despite the important recent drop in CO_2 concentration and gas pressure, monitoring should be maintained in case the gas concentrations and gas pressures return. The evolution of TDG pressure must be followed with a certain frequency to calculate possible CO_2 recharge rates and make accurate predictions. The speed at which gas pressure will recover to pre-degassing values will depend on several factors, including the: (i) input of groundwater recharge at depth, (ii) composition (e.g. pH, metal concentration) and gas content of this groundwater, and (iii) water/rock interaction in the pit walls and adjacent mine tunnels. The pH of the deepest part of the lake, where gas pressure was higher (45-70 m) has not changed significantly during the degassing period (Fig. 7c). Thus, reactivation of carbonate dissolution in this zone is not expected.

In any case, the controlled degassing activity in the lake has provoked drastic changes in the stratification by inducing irreversible changes in the water column with respect to the conditions existing in 2014 (Fig. 7), when the mixolimnion was only 10 m thick and hardly represented 28% of the total lake volume, the rest being occupied by the monimolimion. Today, this proportion has been inverted and the present 41 m thick mixolimnion represents ≈ 80% of the lake volume, while the monimolinion only represents the remaining 20%. This has deep implications for the overall safety of the mine site, since the volume left for potential accumulation of additional CO_2 in the future is now outstandingly less than in 2014, which obviously represents a clear benefit. In any case, the big pipes installed in the pit lake could be reactivated if the gas pressure increases.

Predictive Studies and Long-term Monitoring in Pit Lakes

The Guadiana pit lake case has also revealed the importance of hydrogeochemical research and monitoring programs in flooded mines in general and in pit lakes in particular. This research not only shows important features about the chemistry, limnology, and stratification dynamics of pit lakes with potential use in remediation initiatives, but also can be of great help in predicting future lake evolution and anticipating certain problems before they occur. Geochemical modelling combined with hydrodynamic modelling has proven to be a powerful tool in lake and reservoir managing, and has been successfully applied in AMD-impacted reservoirs and pit lakes (e.g. Delgado et al. 2013; Torres et al. 2016). One-dimensional hydrodynamic-ecological models, such as DYRESM - CAEDYM (e.g. Cui et al. 2016) can be used to investigate the interactions between physical, chemical, and biological processes that occur in pit lakes over different time scales.

More attention should be paid to the accumulation of dissolved gases in deep strata of meromictic pit lakes. Here, the combination of biological activity (e.g. bacterial metabolisms generating CO_2, H_2S, or CH_4) and geochemical processes (e.g. dissolution of carbonates present in wall rocks, sediments and/or wastes dumped in the mine galleries), and hydrogeological dynamics (groundwater inflow carrying dissolved gases) may lead to the storage of these gases and their gradual increase in concentration over time. Quick surveys with gas pressure sensors such as the ones shown in this study (Fig. 12), if repeated with certain frequency (e.g. once a year) should allow one to calculate recharge rates of the gas of concern and predict the possible temporal evolution of gas pressure in a particular pit lake. This problem will probably not exist in circumneutral pit lakes, because in these water bodies dissolved inorganic carbon is chiefly present as bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions, and carbon dioxide is usually negligible (Sánchez-España et al. 2008, 2013). Surveillance should be focused on meromictic acidic pit lakes, especially if carbonates are present in the area. Lime or carbonate addition to neutralize acidity in these pit lakes should be a priori avoided. Thistreatment option should be only considered if the neutralization process can be fast enough to convert all dissolved inorganic carbon to carbonate or bicarbonate species in a relatively short period of time, thus preventing the accumulation of CO_2 at the first stages of low pH (e.g., <5.0-5.5)

Technical Issues when Pumping Metal-rich Acidic Mine Water

A big difference with respect to the degassing operations conducted in volcanic crater lakes like Nyos and Monoun in Cameroon, where lake degassing technology was developed in the 1990s after the tragic limnic eruptions happened in 1984 and 1986 (Halbwachs et al. 2004; Kling et al. 1994, 2005; Tanyileke et al. 2019), is the chemistry of the deep water pumped to the lake surface. The high acidity and metallic content (especially iron) of this water makes it highly corrosive for steel valves, taps, regulators, buoys, and ropes, which are soon covered by thick mineral coatings (Fig. 9c-d). The metallic elements had to be protected with plastic bags to extend their useful life, and were also inspected and cleaned in every control. However, the main disadvantage of bringing the deep water with high metallic load to the surface was the worsening of the water quality compared to pre-degassing conditions. The continuous oxidation of ferrous iron and consequent precipitation of ferric iron has led to significant acidification of the entire mixolimnion and increased metal concentrations (e.g. Zn, Mn; Fig. 10).

The input of arsenic (present at very high concentrations in the deep water; Sánchez-España et al. 2014) was also of some concern. However, the abundant ferric mineral colloids formed in the lake surface (mostly consisting of schwertmannite, which is a well-known adsorbent) prevent the concentration of this element from increasing, since it readily adsorbs to iron precipitates. This has been checked by chemical and electron microscopy analyses (SEM-EDS) of suspended particulate matter sampled in the lake for several seasons (*not shown*).

Several attempts were made to reintroduce the pumped water back to the deep part of the lake by installing 20 m-long plastic cylinders around the pipes. These systems reintroduced a significant part of the pumped water, which progressively sunk to deeper layers by density. However, much of the fountaining water mixed with the pit lake surface, especially in days of strong wind. In any case, considering that the Guadiana mine waters do not have any use and do not mix with local streams, the question of water quality in the upper part of the lake was considered a minor collateral effect that appeared acceptable in view of the benefit of the degassing operations.

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Figure captions

Fig. 1 (a) Satellite view (Google Earth image of the Herrerías mining area, showing the location of Guadiana and Santa Bárbara flooded open pits, and nearby tailings and dams; **(b)** panoramic view of Guadiana acidic pit lake (aerial photograph taken from a drone in 2017).

Fig. 2 Field pictures taken in the Guadiana acidic pit lake during the period 2013-2014: **(a)** Panoramic view of the pit lake taken in December 2013, when it still showed a greenish colour in the water surface as a result of an upper layer with relatively low Fe(III) content and the presence of green algae; **(b)** Detail of the Van Dorn sampling bottle after collecting CO_2-charged water from the deep part (60 m); **(c-d)** Field work with simultaneous physico-chemical profiling with multiparametric probes and gas sampling in gas-tight sampling bags; **(e-h)** Sequence of pictures showing the installation and activation of the first pilot-scale pipes in October 2014.

Fig. 3 Field pictures taken in the Guadiana acidic pit lake during the period 2017-2018: **(a)** Activation of degassing Pipe 1; **(b)** installation of degassing Pipe 2; **(c)** Conventional high-speed motor pump initially used for pumping of degassing Pipe 2, which probed to be inefficient to pump the gas-charged deep water; **(d-e)** Membrane pumps finally used to evacuate the gas-charged water from within the hoses and put degassing pipes 1 and 2 into operation; **(f)** Detail of mine tunnel and big fracture in the pit walls at the northern part of the open pit; **(g)** Remnants of drill cores found in the pit with abundant carbonate (calcite, dolomite) present in fractures and voids of the volcanic rocks; **(h-i)** Warning signboards installed in the pit fence after the activation of Pipe 1.

Fig. 4 Sequence of pictures showing the different pipes installed in Guadiana pit lake in chronological order: **(a)** Prototype 1; **(b)** Prototype 2; **(c)** Pipe 1; **(d)** Pipe 2; **(e)** Pipes 1 and 2 working simultaneously. The hose diameter, height of the resulting fountain, initial flow rate, and date of installation are indicated.

Fig. 5 Vertical evolution of total dissolved gas (TDG) pressure in Guadiana pit lake: **(a)** TDG profiles obtained directly with a TDG Hach sensor; **(b)** TDG profiles calculated from gas volume measurements (October 2014 and April 2015), Pro Oceanus mini-TDG probe (September 2017) and TDG Hach sensor (all other dates).

Fig. 6 (a) Temporal evolution of total dissolved gas (TDG) pressure (in bars) at different depths of Guadiana pit lake during the degassing period from October 2014 to May 2019; **(b)** Volume of carbon dioxide (CO_2, in m^3) extracted during the degassing period.

Fig. 7 Depth profiles of selected physico-chemical parameters taken in the Guadiana acidic pit lake in the period from December 2013 to May 2019, showing the temporal evolution of the lake stratification during the degassing activities: **(a)** Temperature (T, in ° C); **(b)** Specific conductance (in µS/cm); **(c)** pH; **(d)** Oxidation-reduction potential (ORP, in mV).

Fig. 8 (a-d) Schematic diagram showing the evolution of Guadiana pit lake during the last four years as a result of controlled degassing; **(e)** Idealized cross-section of the whole Guadiana mine complex, including the open pit as well as the set of sub-horizontal mine galleries and vertical shafts which are hydraulically connected with the pit; numbers next to the mine pit and galleries refer to depths (in meters) below the topographic surface (modified from Pinedo Vara 1962).

Fig. 9 Sequence of pictures showing the effects of the continuous pumping of gas-charged deep water to the pit lake surface: **(a)** Aspect of the pit lake in April 2014, before the start of degassing; **(b)** Aspect of the pit lake in April 2015, after six months of deep water pumping by two pilot-scale pipes; **(c-d)** Aspect of the degassing pipes (Prototypes 1 and 2) after two years of operation (note massive formation of mineral coatings on the tap, foam platform and buoys); **(e)** panoramic view of the pit lake in June 2018 (note deep red colour resulting from high contents of dissolved Fe[III]).

Fig. 10 (a) Depth profiles of dissolved oxygen (DO, as percent saturation) taken in Guadiana pit lake in the period from December 2013 to May 2019; **(c-d)** Depth profiles of metal concentration (all in mg/L) from June 2010 to Dec 2017: total iron (Fe_{tot}. b), zinc (Zn, c), manganese (Mn, d).

Fig. 11 Plots showing the stabilization time of total dissolved gas pressure in two different moments and with two different measuring instruments: **(a)** Profile conducted in September 2017 with a Mini-TDG (Pro Oceanus, Bridgewater, Oceanus); **(b)** Profile conducted in June 2018 with a TDG sensor from Hach connected to a Hydrolab MS5 multiparametric probe.

Fig. 12 Depth profiles of total dissolved gas [TDG] pressure in some Spanish pit lakes in the Iberian Pyrite Belt (Guadiana, La Zarza, Filón Centro, Cueva de la Mora, San Telmo) and La Unión mines (Brunita). In all cases, we indicate the date the profiles were taken, the atmospheric equilibrium pressure (= 1 bar), the absolute pressure (for reference), and the minimum difference (Δp) between the TDG pressure and the absolute pressure at that depth.

Table 1. Chronological sequence of some relevant measures and milestones achieved in Guadiana pit lake for the period 2008-2019.

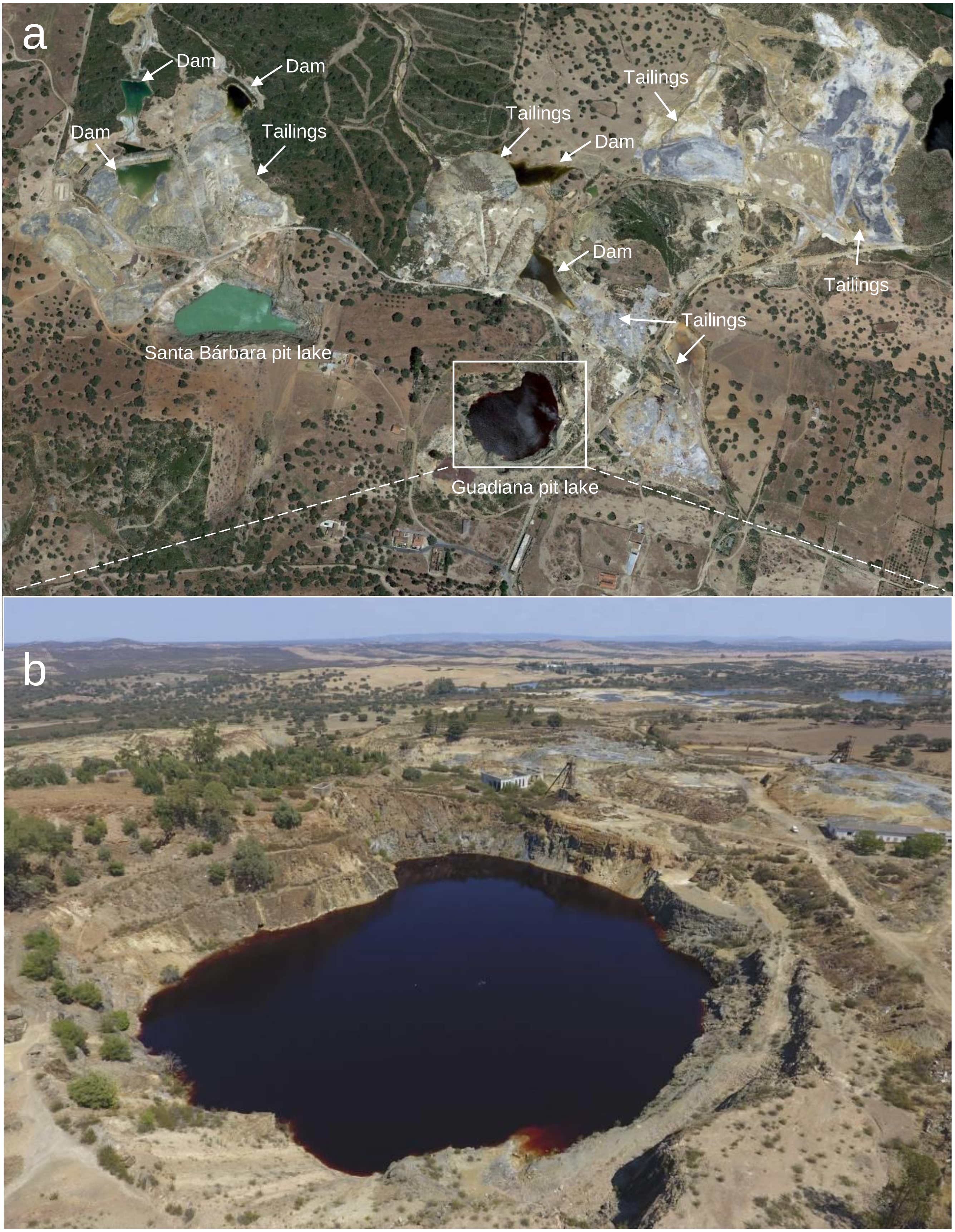
Date	Action	Comments
March 2008	First visit to the pit lake, water sampling and chemical results	Observation of elevated gas pressure and abundant bubbles in deep water sampled from monimolimnion (40 m)
June 2010	First full-scale survey with bathymetric studies, nutrient and DIC measurement	First results on DIC concentration, which yielded elevated values exceeding 3200 mg/L CO_2; impossible to obtain accurate depth readings and intact sediment cores due to elevated gas pressure at depth
March 2012	First isotopic analyses of pit lake water and surrounding rocks and plants	Results strongly suggestive of DIC being derived by carbonate dissolution
Sept 2013	Rock dissolution experiments conducted with different rock types from Guadiana mine	Chemical/mineralogical analyses indicate abundant presence of carbonates in spilitic rocks and experimental results clearly show a fast carbonate dissolution at pH <4.5-5.0
Dec 2013	First accurate measurement of gas pressure and concentration at depth with gas-sampling bags	Precise quantification of CO_2 concentration, giving values approaching 5000 mg/L CO_2 and partial pressure (pCO_2) of 3.6 bars
March 2014	First comprehensive study published and regional authorities contacted	The scientific community is aware of a new case of a gas-charged lake with potential safety risk
April 2014	First pilot-scale pipe installed in the pit lake	Thin hose (19 mm) diameter 60 m long installed, but flow initiation failed due to insufficient pump power
Oct 2014	Second pilot-scale installed in the pit lake	A second pipe, 32 mm in diameter and 61 m is installed; both pipes are set in operation with a stronger pump
April 2016	Second study reporting results of two years of pilot-scale pipes performance is published	Big impact in media provokes alarm in local population; contacts and negotiations with regional authorities
June 2017	Contract signed between Spanish Geological Survey and the Bureau of Mines of the Andalusian Government	Installation of a larger pipe (61 m long and 50 mm diameter) in pit lake center, giving flow rate of 50 L/min

Oct 2018	Installation of a second pipe	A new pipe (65 m long and 63 mm diameter) installed in June 2018, starts operating at a flow rate of 60 L/min
Nov 2018	Removal of reductions in both pipes	Reductions at the discharge points of both pipes removed to increase flow rate. The combined discharge increases to 113 L/min
May 2019	Last monitoring campaign for evaluation of degassing program	Both pipes gradually decrease in height and flow rate due to diminished gas pressure at depth. Pipe 1 stops working Feb 2019; Pipe 2 is exhausted May 2019

Table 2. Summary of degassing pipes installed in the Guadiana acidic pit lake during the period 2014-2019, with some relevant features indicated.

Pipe	Date installed	External diameter (mm)	Internal diameter (mm)	Hose length (m)	Fountain height (m)	Flow rate (L/min)	Operation time (months)
Prototype 1	April 2014	25	19	60	0.35	2	18
Prototype 2	Oct 2014	40	32	61	1.4	10	48
Pipe 1	Sept 2017	50	42	61	3.0	50	17
Pipe 2	June 2018	63	55	65.5	3.5	60	8

Figure 1



a
Dam
Dam
Dam
Tailings
Tailings
Tailings
Dam
Dam
Tailings
Tailings
Santa Bárbara pit lake
Guadiana pit lake
b

Figure 2

Figure 3


a
b
c
d
e
f
g
HCl
h
PROHIBIDO EL PASO
MOTIVO:
PROHIBIDO EL PASO
POR MOTIVOS DE
SEGURIDAD MINERA
PROHIBIDO EL PASO
MOTIVO:
i
Proyecto de Desgasificación controlada de la Corta Guadiana con alta presión de CO2 disuelto

Figure 4

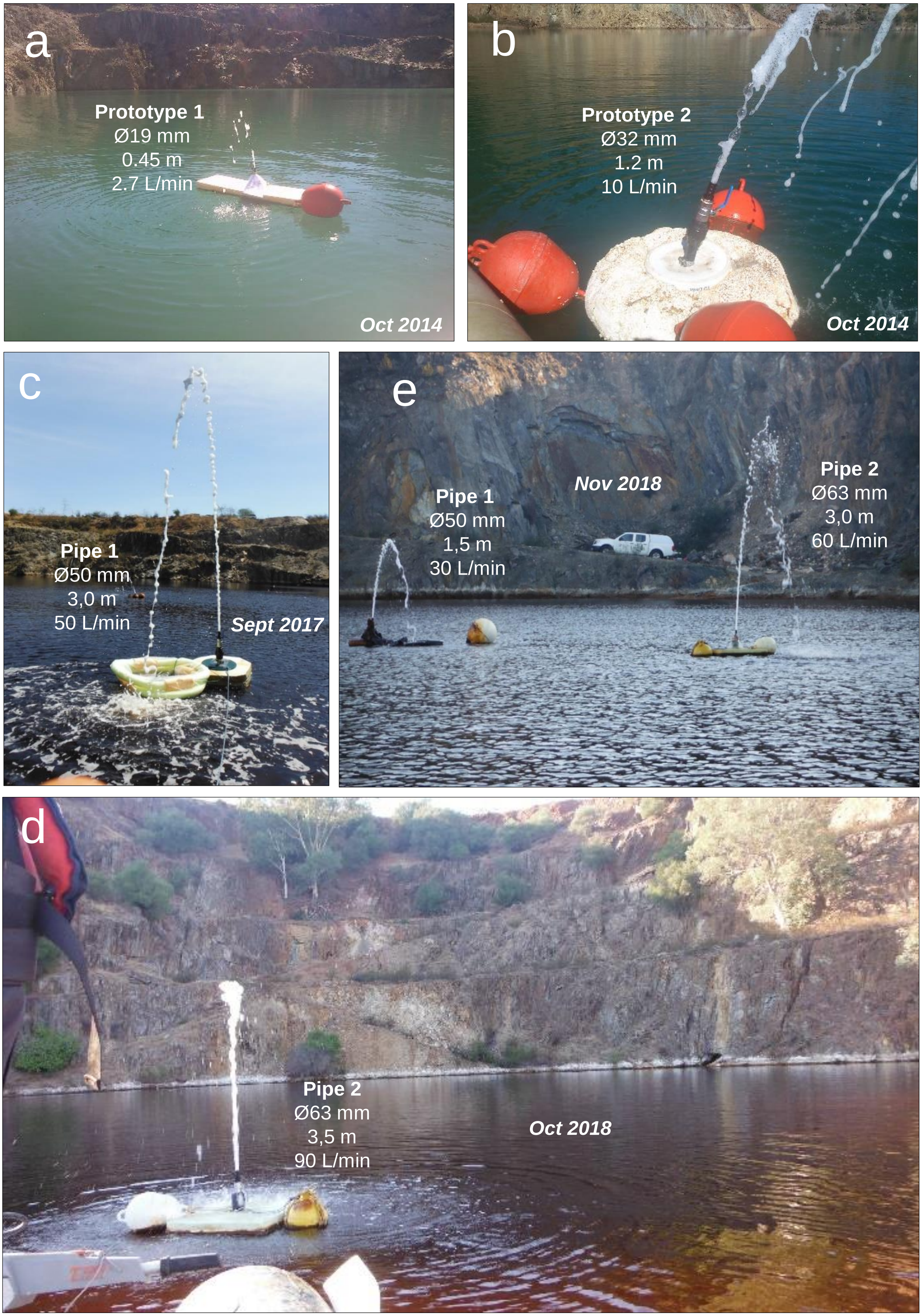

a
Prototype 1
Ø19 mm
0.45 m
2.7 L/min
Oct 2014
b
Prototype 2
Ø32 mm
1.2 m
10 L/min
Oct 2014
c
Pipe 1
Ø50 mm
3,0 m
50 L/min
Sept 2017
e
Nov 2018
Pipe 1
Ø50 mm
1,5 m
30 L/min
Pipe 2
Ø63 mm
3,0 m
60 L/min
d
Pipe 2
Ø63 mm
3,5 m
90 L/min
Oct 2018

Figure 5

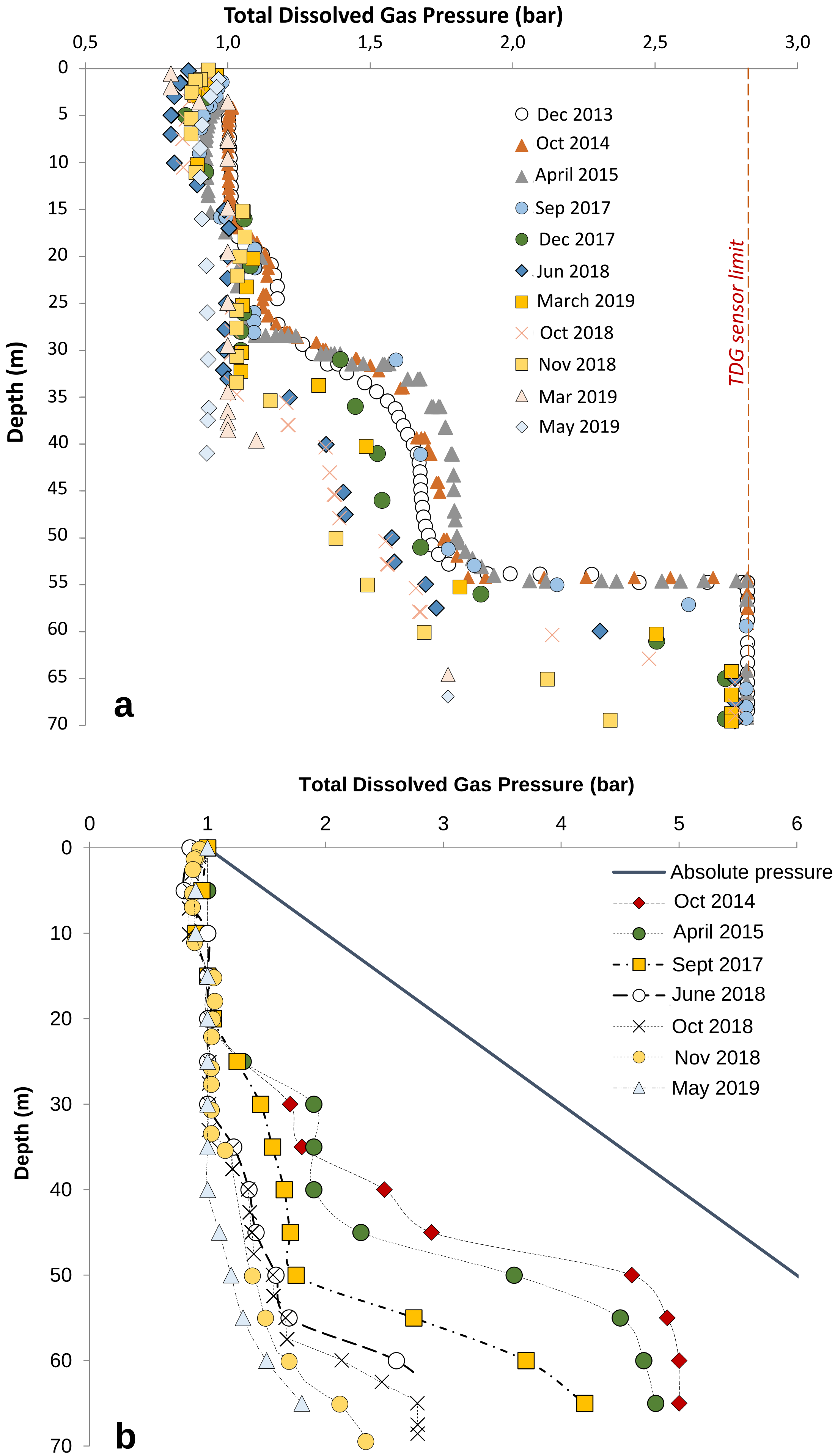

Total Dissolved Gas Pressure (bar)
0,5
1,0
1,5
2,0
2,5
3,0
Depth (m)
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
Dec 2013
Oct 2014
April 2015
Sep 2017
Dec 2017
Jun 2018
March 2019
Oct 2018
Nov 2018
Mar 2019
May 2019
TDG sensor limit
a
Total Dissolved Gas Pressure (bar)
0
1
2
3
4
5
6
Depth (m)
0
10
20
30
40
50
60
70
Absolute pressure
Oct 2014
April 2015
Sept 2017
June 2018
Oct 2018
Nov 2018
May 2019
b

Figure 6

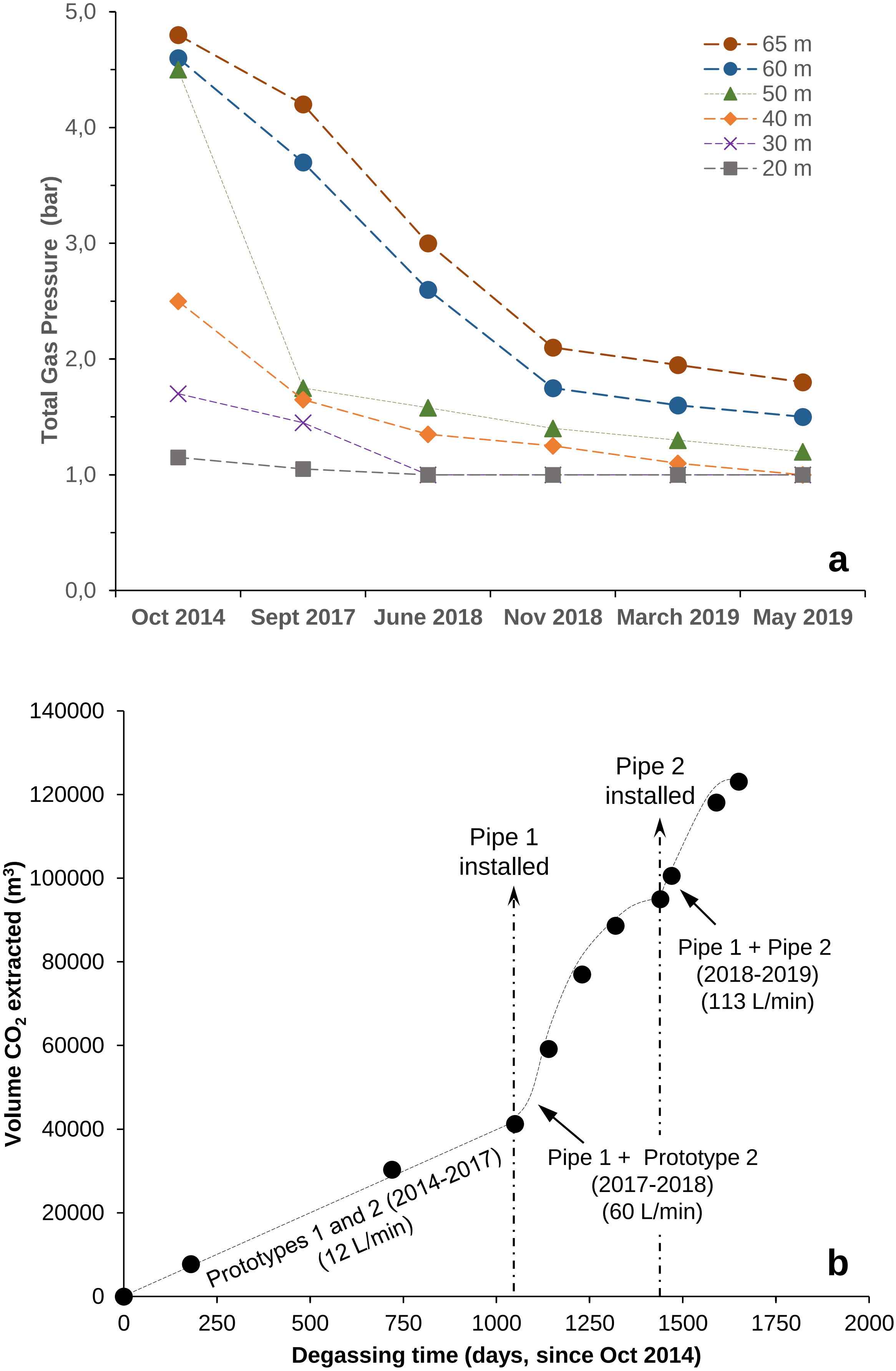
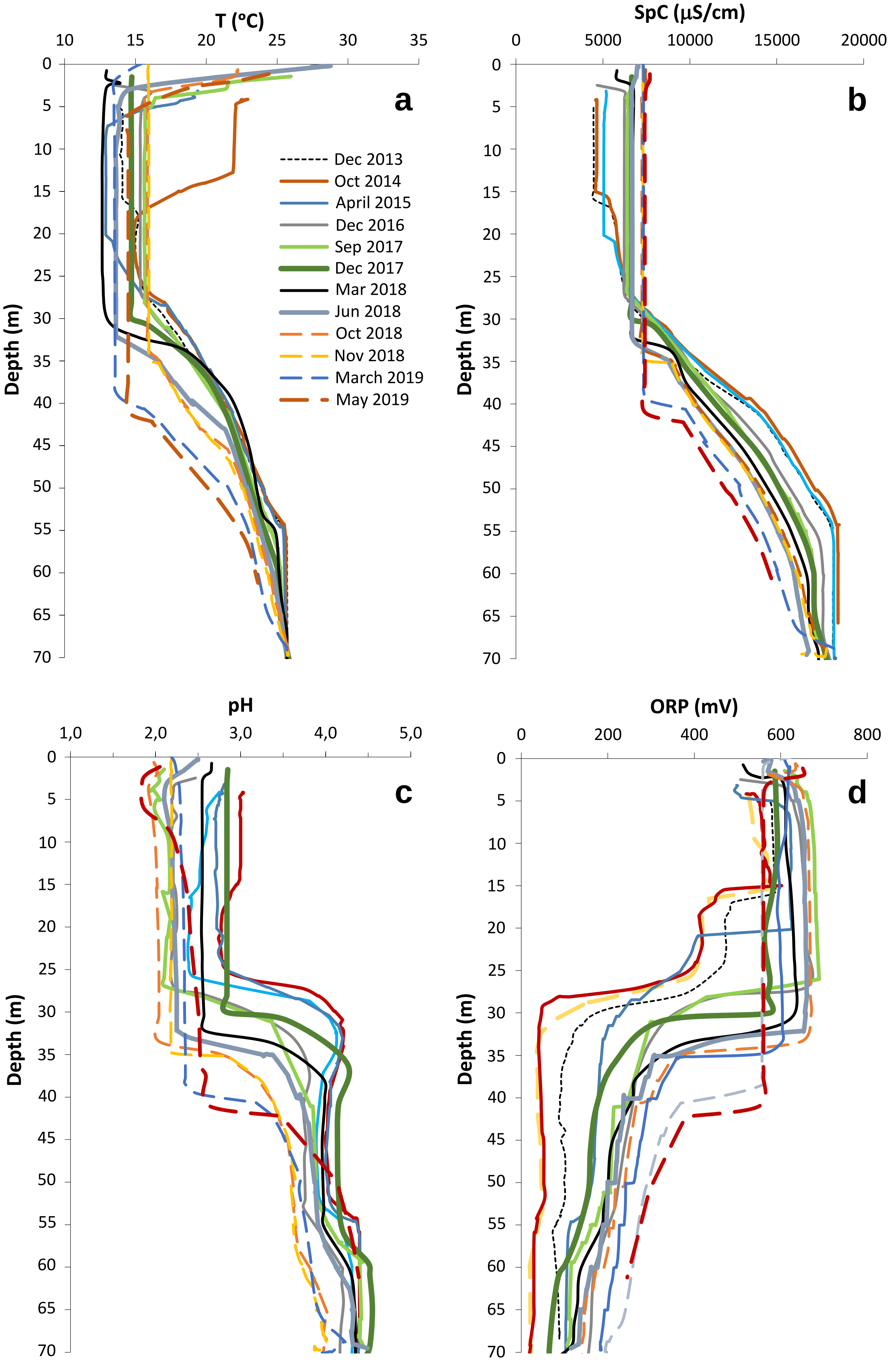

5,0
4,0
3,0
2,0
1,0
0,0
Total Gas Pressure (bar)
65 m
60 m
50 m
40 m
30 m
20 m
Oct 2014
Sept 2017
June 2018
Nov 2018
March 2019
May 2019
a
140000
120000
100000
80000
60000
40000
20000
0
Volume CO_2 extracted (m^3)
0
250
500
750
1000
1250
1500
1750
2000
Degassing time (days, since Oct 2014)
Pipe 2 installed
Pipe 1 installed
Pipe 1 + Pipe 2 (2018-2019) (113 L/min)
Pipe 1 + Prototype 2 (2017-2018) (60 L/min)
Prototypes 1 and 2 (2014-2017) (12 L/min)
b

Figure 7



T (ºC)
10
15
20
25
30
35
a
Depth (m)
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
Dec 2013
Oct 2014
April 2015
Dec 2016
Sep 2017
Dec 2017
Mar 2018
Jun 2018
Oct 2018
Nov 2018
March 2019
May 2019
SpC (µS/cm)
0
5000
10000
15000
20000
b
pH
1,0
2,0
3,0
4,0
5,0
c
ORP (mV)
0
200
400
600
800
d

Figure 8

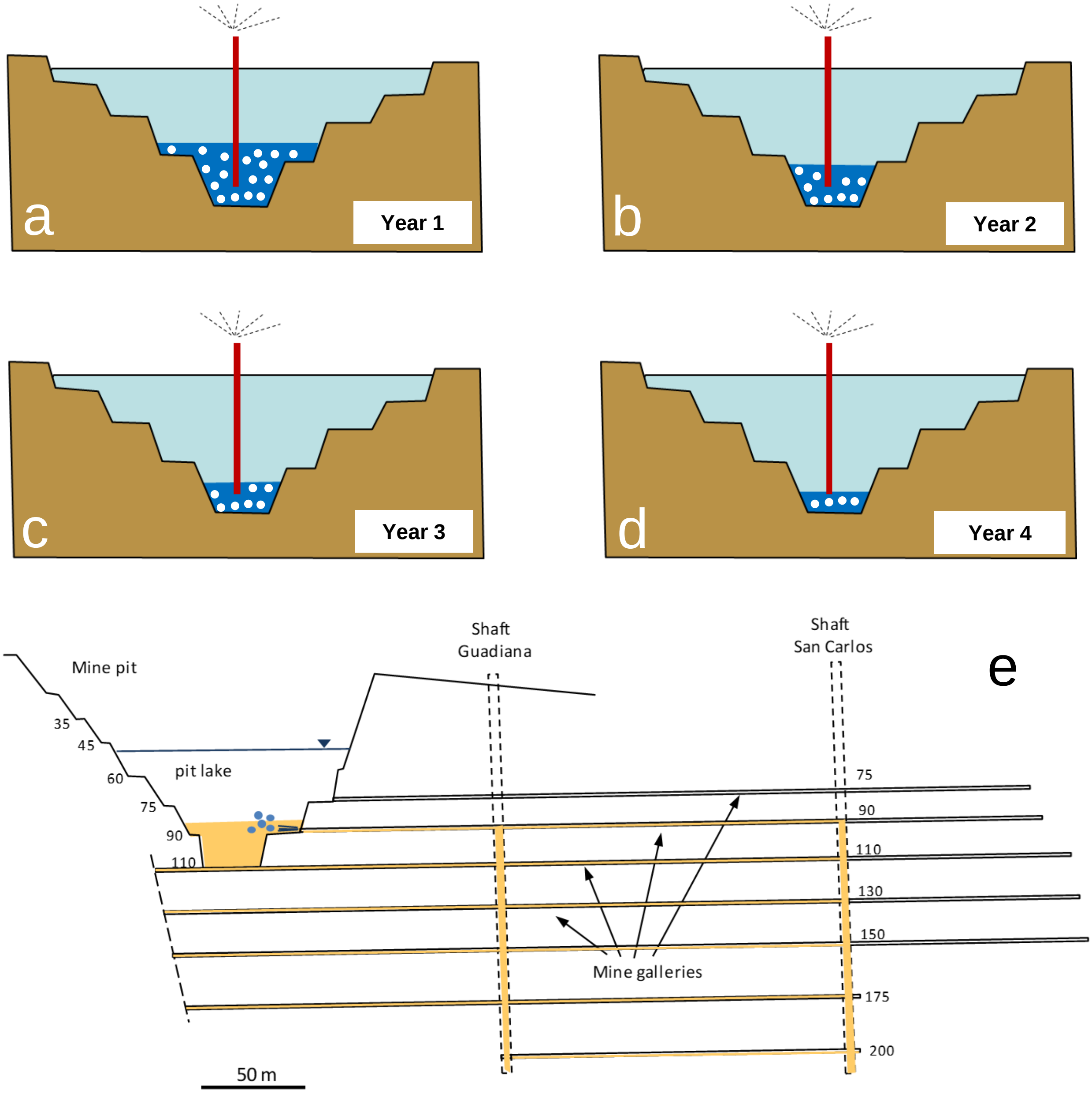

a
Year 1
b
Year 2
c
Year 3
d
Year 4
e
Shaft
Guadiana
Shaft
San Carlos
Mine pit
35
45
60
75
90
110
pit lake
75
90
110
130
150
175
200
Mine galleries
50 m

Figure 9

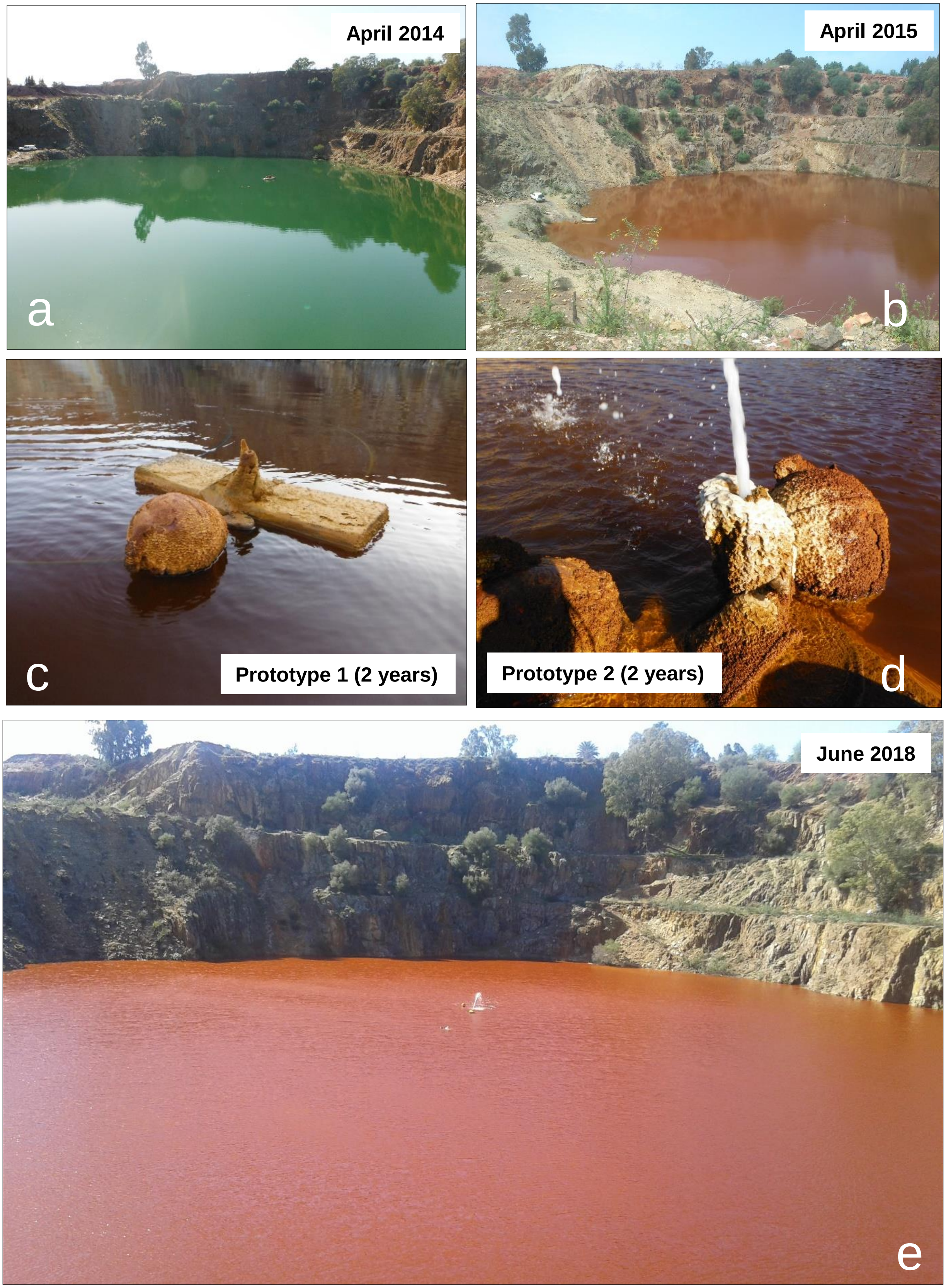

April 2014
a
April 2015
b
c
Prototype 1 (2 years)
Prototype 2 (2 years)
d
June 2018
e

Figure 10

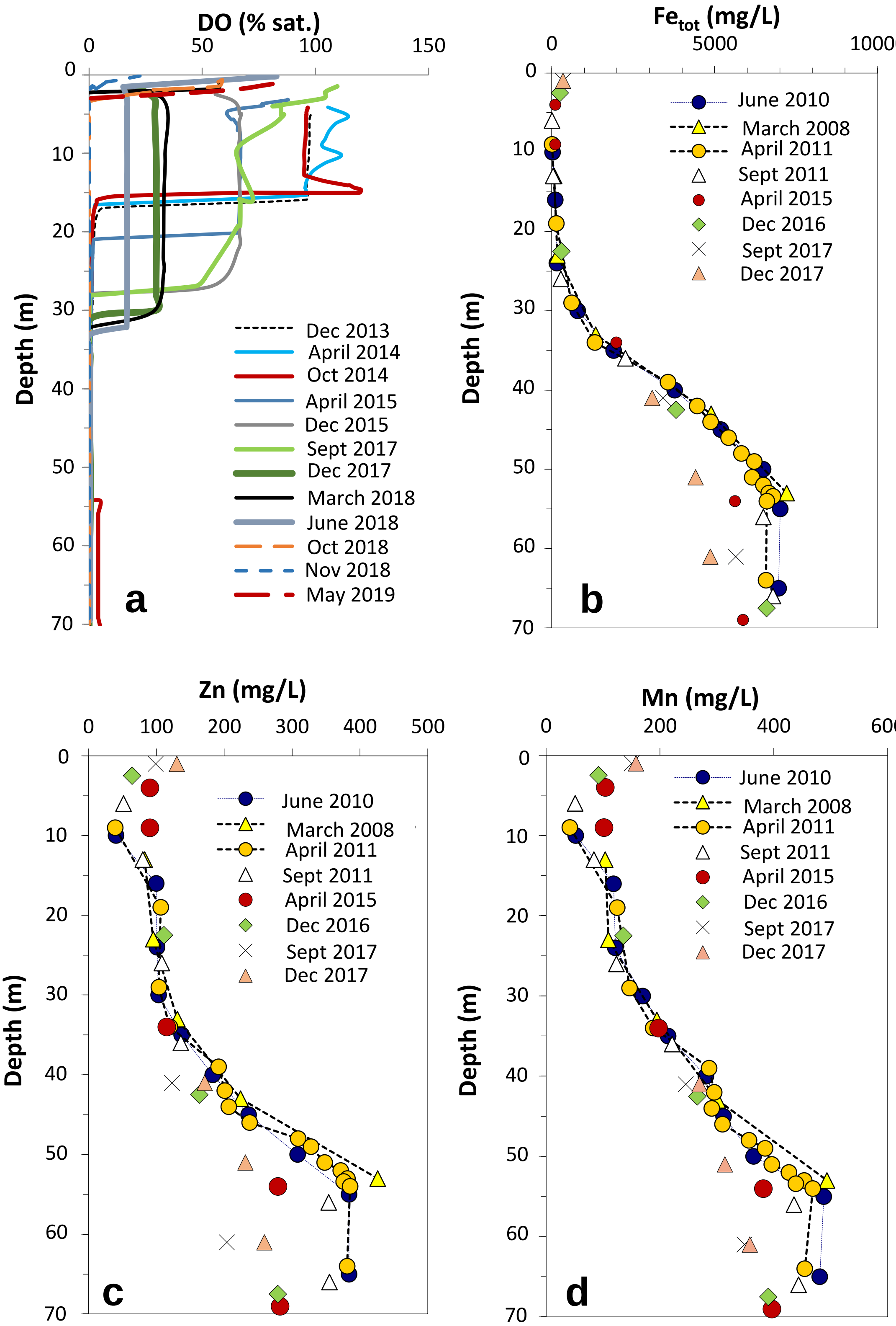

DO (% sat.)
0
50
100
150
Depth (m)
0
10
20
30
40
50
60
70
Dec 2013
April 2014
Oct 2014
April 2015
Dec 2015
Sept 2017
Dec 2017
March 2018
June 2018
Oct 2018
Nov 2018
May 2019
a
Fe$_{tot}$ (mg/L)
0
5000
10000
Depth (m)
0
10
20
30
40
50
60
70
June 2010
March 2008
April 2011
Sept 2011
April 2015
Dec 2016
Sept 2017
Dec 2017
b
Zn (mg/L)
0
100
200
300
400
500
Depth (m)
0
10
20
30
40
50
60
70
June 2010
March 2008
April 2011
Sept 2011
April 2015
Dec 2016
Sept 2017
Dec 2017
c
Mn (mg/L)
0
200
400
600
Depth (m)
0
10
20
30
40
50
60
70
June 2010
March 2008
April 2011
Sept 2011
April 2015
Dec 2016
Sept 2017
Dec 2017
d

Figure 11

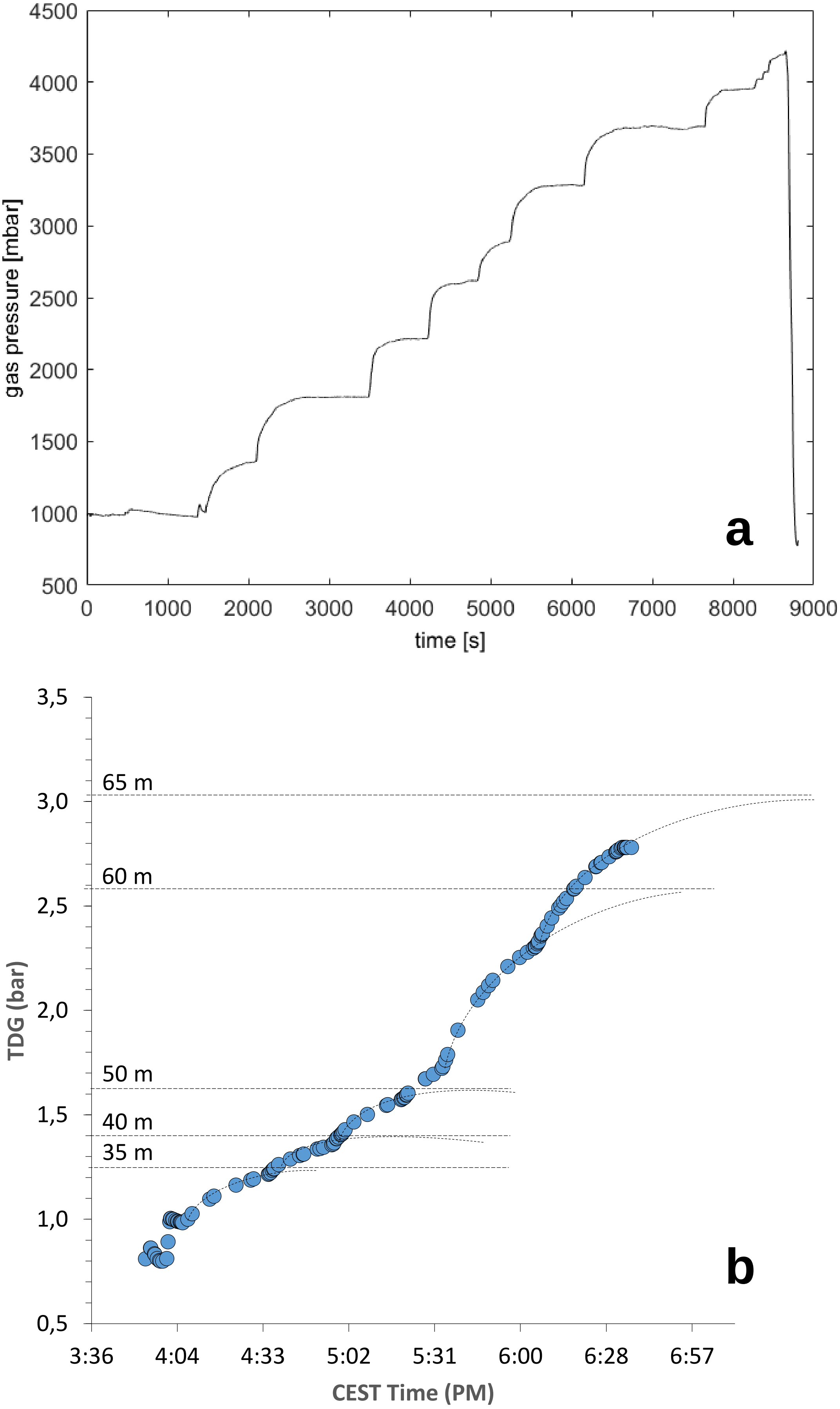
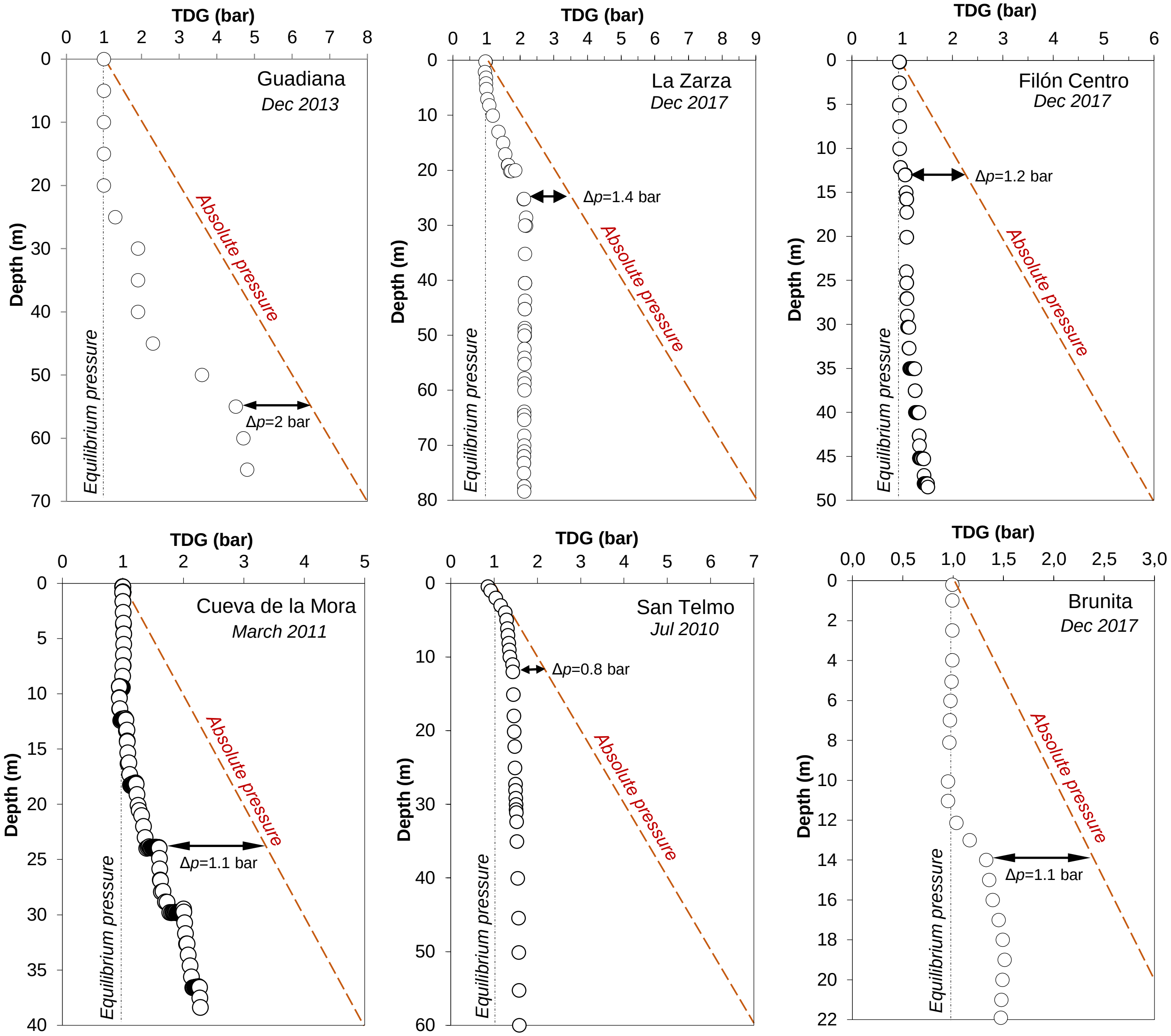

gas pressure [mbar]
4500
4000
3500
3000
2500
2000
1500
1000
500
0
1000
2000
3000
4000
5000
6000
7000
8000
9000
time [s]
a
TDG (bar)
3,5
3,0
2,5
2,0
1,5
1,0
0,5
65 m
60 m
50 m
40 m
35 m
3:36
4:04
4:33
5:02
5:31
6:00
6:28
6:57
CEST Time (PM)
b

Figure 12


TDG (bar)
Depth (m)
Guadiana
Dec 2013
Equilibrium pressure
Absolute pressure
Δp=2 bar
La Zarza
Dec 2017
Δp=1.4 bar
Filón Centro
Dec 2017
Δp=1.2 bar
Cueva de la Mora
March 2011
Δp=1.1 bar
San Telmo
Jul 2010
Δp=0.8 bar
Brunita
Dec 2017
Δp=1.1 bar
0
1
2
3
4
5
6
7
8
9
10
20
30
40
50
60
70
80
15
25
35
45
0,0
0,5
1,0
1,5
2,0
2,5
3,0
12
14
16
18
22