Supplementary material

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1 Data availability

Data for this paper is available in the Hplus database by following the permanent link `https://hplus.ore.fr/en/osorio-leon-et-al-2022-wrr-data`

2 Input compositions of water and rock for the base case simulation with the numerical model

Table 1. Input water composition for the numerical model

Temperature [ºC]	16	
pH	7	
	Concentrations	[mol/kg]
$O_2(aq)$		2.6×10^{-2}
Cl^-		1.9×10^{-3}
SO_4^{2-}		3.0×10^{-4}
Na^+		2.2×10^{-3}
Mg^{2+}		5.3×10^{-4}
Al^{3+}		8.9×10^{-8}
H_4SiO_4		2.2×10^{-4}
K^+		9.2×10^{-5}
Ca^{2+}		2.5×10^{-4}
Fe^{2+}		0.0
$CO_2(aq)$		4.3×10^{-5}

3 Mineral stability diagram

4 Dissolved iron measurements

Major and trace cations were quantified by Inductively Coupled Plasma Mass Spectroscopy (Agilent Technologies, 7700x) in pre-acidified and 0.2 μm-filtered samples. Uncertainties were between 2 to 5%. Major anion samples (non-acidified) were analyzed by Ionic Chromatography (Dionex DX-120) with uncertainties below 4%. Groundwater sampling consisted on descending a submersible MP1 pump (Grundfos) until the depth of the dominant fracture in the borehole. Physicochemical parameters in the pump discharge were monitored with a WTW probe. Groundwater was sampled after the monitored parameters were stable.

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Table 2. Mineralogical composition used as input for the numerical simulations. *Diss Only* indicates that only dissolution is allowed and *tst* indicates that both dissolution and precipitation can occur. Kinetic and thermodynamic parameters for Equation (4) are taken from the database files of the Thermoddem project (Blanc et al., 2012) and from Palandri and Kharaka (2004).

Mineral	Structural formula	Mineral volume fraction [Φ_j]	Reaction type
Primary minerals			
Albite	$NaAlSi_3O_8$	0.000	TST - Diss only
Quartz	SiO_2	0.444	TST - Diss only
K-Feldspar	$KAlSi_3O_8$	0.297	TST - Diss only
Biotite	$K(Mg_2Fe^{II})(Si_3Al)O_{10}(OH)_2$	0.099	TST - Diss only
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$	0.149	TST - Diss only
Secondary minerals			
Chlorite	$(Mg_3Fe_2^{II}Al)(Si_3Al)O_{10}(OH)_8$	1×10^{-5}	TST
Kaolinite	$Al_2Si_2O_5(OH)_4$	0.000	TST
Goethite	$Fe^{III}OOH$	0.000	TST

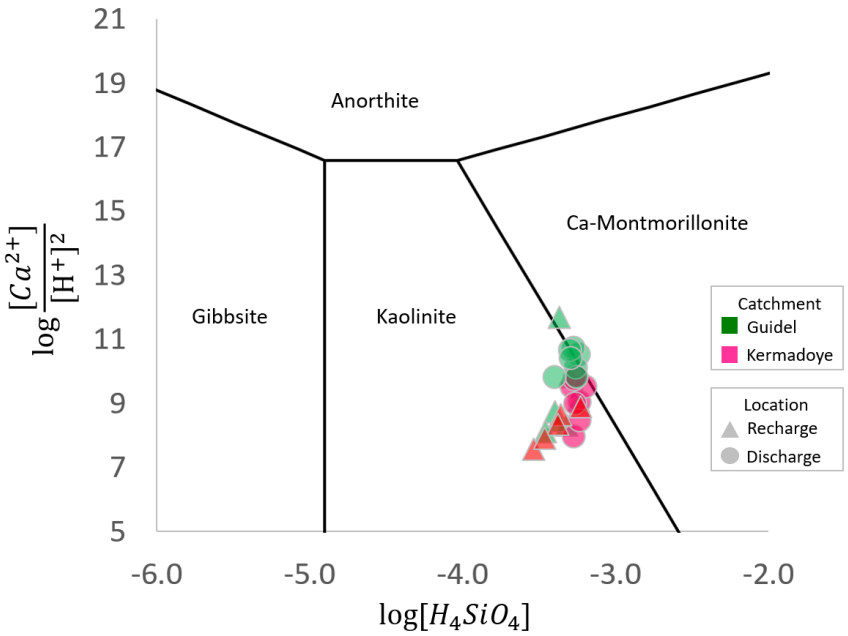


Figure 1. Mineral stability diagram

5 Depth of the groundwater reservoir

Since fracture networks are highly heterogeneous features (Le Borgne et al., 2006), one cannot directly rely the depth of an intersected fracture in a borehole with the representative depth of the circulating fluid's reservoir. For instance, at the site scale, normal faults dipping of about 70º (Ruelleu et al., 2010) will globally favor subvertical circulations. At a more restricted scale, a fracture analysis in a borehole from the Guidel catchment (Bochet et al., 2020) has shown that fracture's dip can vary from 20 to 80º.

Following this, we have used the groundwater's temperature as a proxy of depth. Hence, the depth of the reservoir of the groundwater circulating in a fracture ($Depth_{proxy}$) was calculated as:

$$Depth_{proxy} = \frac{T - T_{rech}}{G_G}$$

T corresponds to groundwater temperature as measured from borehole logs, T_{rech} corresponds to the average recharge temperature of the Ploemeur site, that is 12 ºC, as deduced from the average temperature in the weather station, and G_G corresponds to the Geothermal Gradient. For the Ploemeur site, G_G has been considered as 0.013 $°C.m^{-1}$ after (Pouladi et al., 2021).

6 Sensitivity of $Depth_{proxy}$ estimates

We note that the depth estimates for the DO measurements presented in Figure 7 rely on using groundwater's temperature as a proxy for depth ($Depth_{proxy}$). As estimated, $Depth_{proxy}$ depends on two site-dependent parameters, i.e. the average recharge temperature (T_{rech}) and the Geothermal Gradient (G_G). Both parameters are mostly invariant at short timescales and are not easily measurable. As a result, uncertainties around their value come from measurements rather than seasonality or natural disturbances. The CZO of Ploemeur is a well-studied site and both T_{rech} and G_G are well constrained, allowing to reduce incertitude's around their value. The average value for T_{rech} has been estimated to be 12.2±0.41 $°C$ as deduced from temperature time-series (from 2002 to 2018) recorded at the weather station in the Ploemeur CZO. On the other hand, previous works suggest that the G_G of the Ploemeur site ranges between 0.016 and 0.013 $°C.m^{-1}$ (Pouladi et al., 2021; Klepikova et al., 2011) and for this work we considered the most recent estimate of 0.013 $°C.m^{-1}$ after Pouladi et al. (2021).

It is important to notice that the estimated $Depth_{proxy}$ is highly sensitive to both parameters and it can thus directly impact the estimated depth of the oxygenated zone in the aquifer. For instance, if one considers the borehole with the highest temperature (and thus the deepest $Depth_{proxy}$) from Figure 7 (from main text), and by combining the uncertainties of T_{rech} and G_G , the maximum depth in which oxygen has been detected in this study can oscillate between 333 m and 473 m below surface.

6.1 Effect of velocity on oxic iron concentrations

Figure 2 shows how, for a same Damköhler number, the variations in the apparent vertical velocity impacts the iron concentrations at oxic conditions according to Equation 19 in main text. Predicted concentrations are restricted to low values because they are limited by the fast oxidation of iron by oxygen. Note that they are close to the detection limit of ICPMS analysis that usually is close to 10^{-4} ppb. This makes difficult to constrain the apparent vertical velocity by using the iron concentration data, yet it is possible if analytical methods for iron are sensible enough.

7 Borehole logs

7.1 Methods

Multiparameter borehole logs under ambient conditions (dissolved oxygen, temperature, electrical conductivity and pH) acquired since 2003, available in the database of the French network of hydrogeological research sites (`https://hplus.ore.fr/en/`), were used as base for exploring the physicochemical parameters with depth. This dataset was completed with two additional field campaigns in order to validate the historical data. Multiparameter borehole logs in ambient conditions were acquired at two different times of the hydrologic year: high groundwater level's season (late fall 2022) and low level's season (late spring 2021) using an Idronaut Ocean Seven multiparameter probe. The instrument was calibrated following the manufacturer's specification and the accuracy of

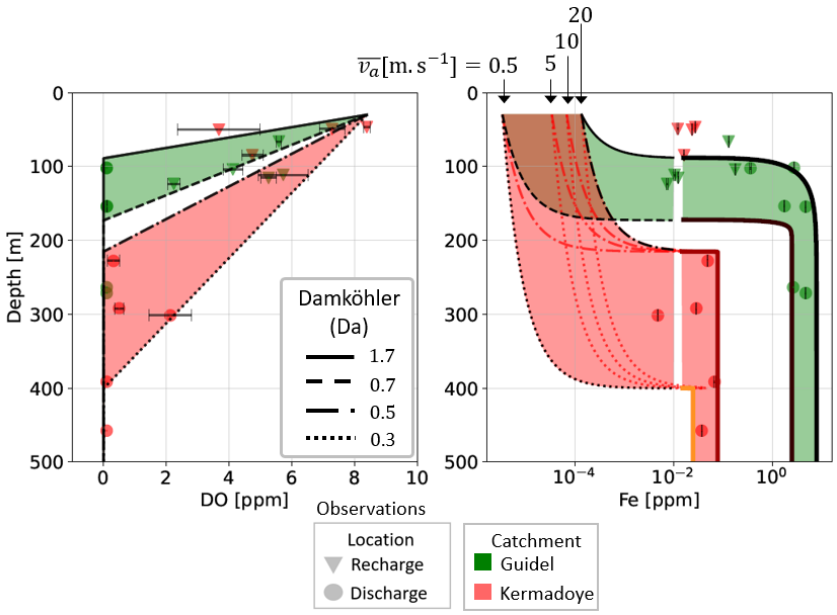


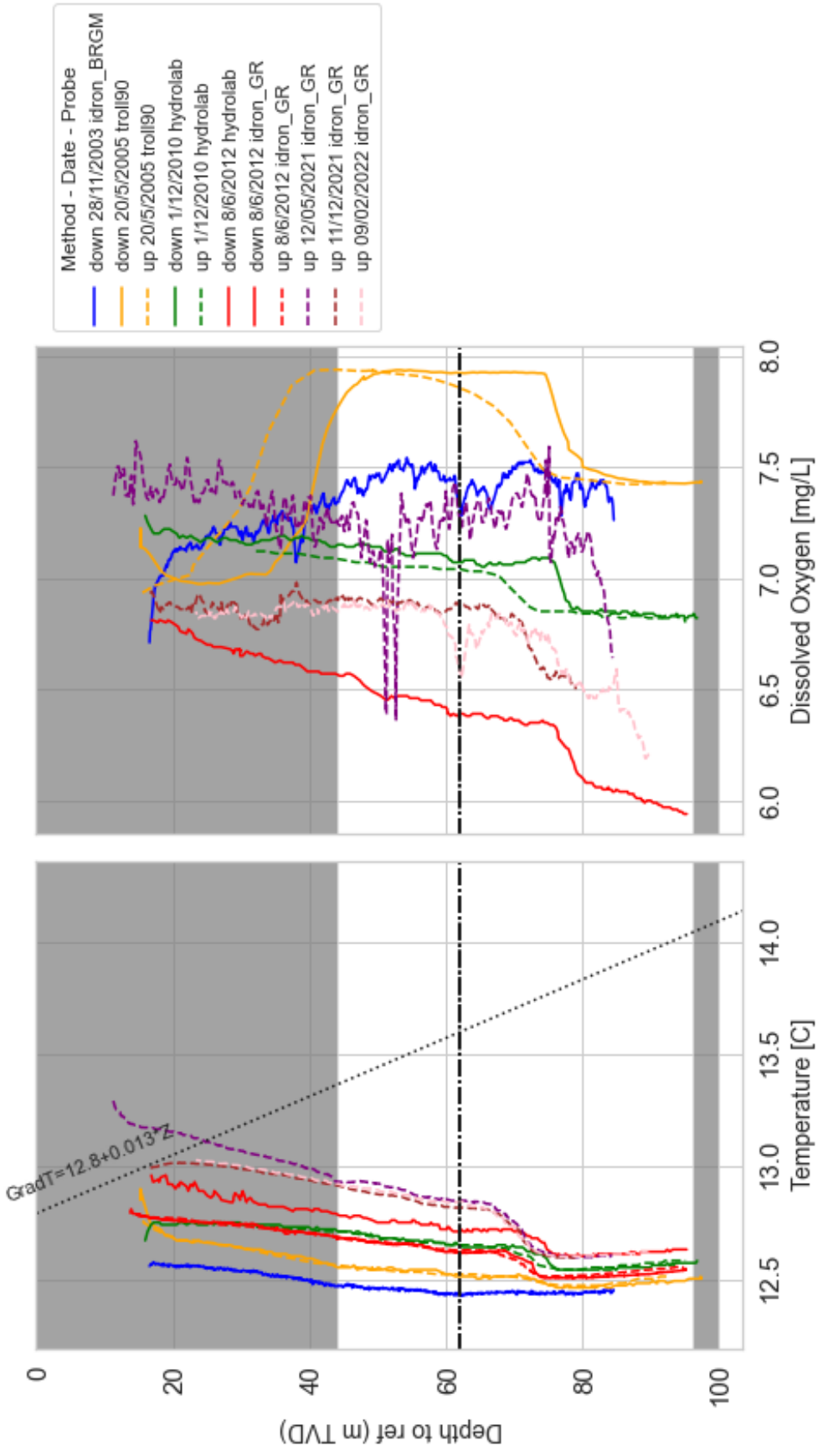
Figure 2. Effect of vertical velocity on the predicted iron concentrations at oxic concentrations

the DO probe ($\pm$ 0.1 $mg.L^{-1}$) was crosschecked by gas chromatography analyses at the University of Rennes 1 (Figure 3).

7.2 logs per borehole

The following figures present the synthesis of multiparameter logs for every borehole. The shaded areas correspond to the tubewall while the white areas correspond the slotted sections. The horizontal dash-dotted lines correspond to fractures intersected in the borehole (black for the main fracture, grey for secondary fractures).

The legend in every plot indicate the mode of log-acquisition ("up" for upwards, down for "downwards"), the date, and the name of the multiparameter probe.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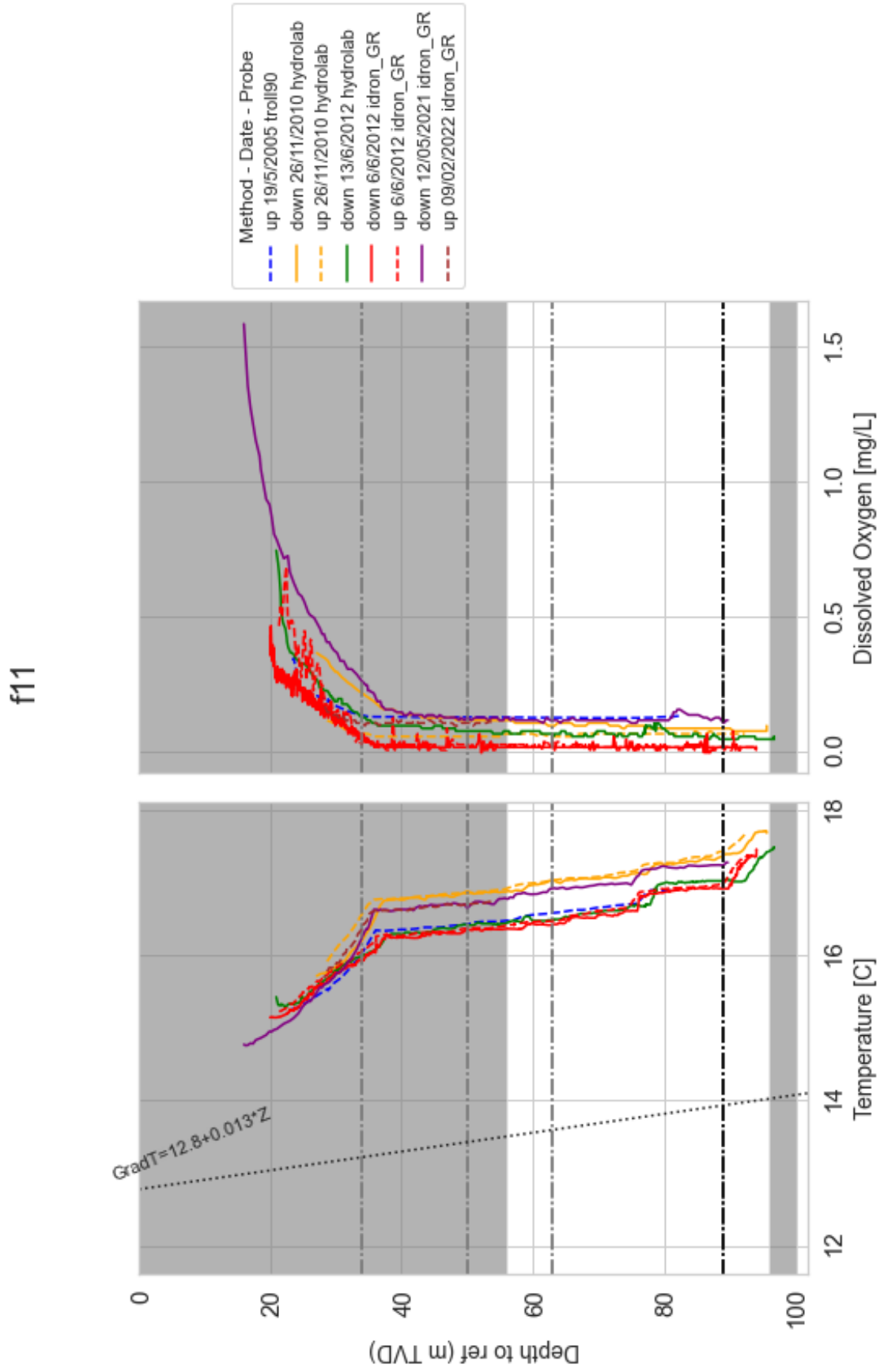
down 28/11/2003 idron_BRGM
down 20/5/2005 troll90
up 20/5/2005 troll90
down 1/12/2010 hydrolab
up 1/12/2010 hydrolab
down 8/6/2012 hydrolab
down 8/6/2012 idron_GR
up 8/6/2012 idron_GR
up 12/05/2021 idron_GR
up 11/12/2021 idron_GR
up 09/02/2022 idron_GR
Dissolved Oxygen [mg/L]
6.0
6.5
7.0
7.5
8.0
Temperature [C]
12.5
13.0
13.5
14.0
GradT=12.8+0.013*Z
Depth to ref (m TVD)
0
20
40
60
80
100

f9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Method - Date - Probe
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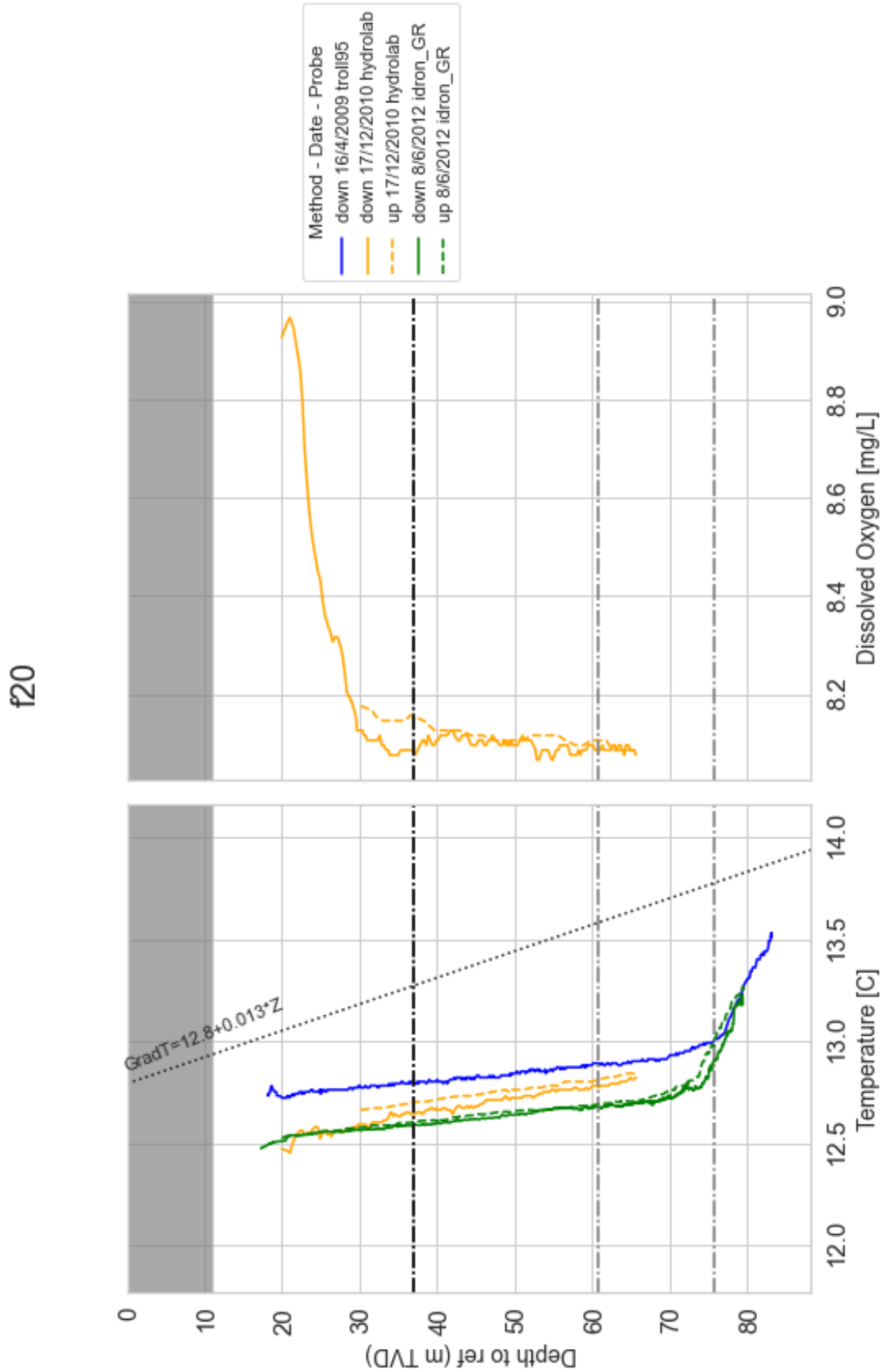
down 26/11/2010 hydrolab
up 26/11/2010 hydrolab
down 13/6/2012 hydrolab
down 6/6/2012 idron_GR
up 6/6/2012 idron_GR
down 12/05/2021 idron_GR
up 09/02/2022 idron_GR
Dissolved Oxygen [mg/L]
0.0
0.5
1.0
1.5
Temperature [C]
12
14
16
18
GradT=12.8+0.013*Z
Depth to ref (m TVD)
0
20
40
60
80
100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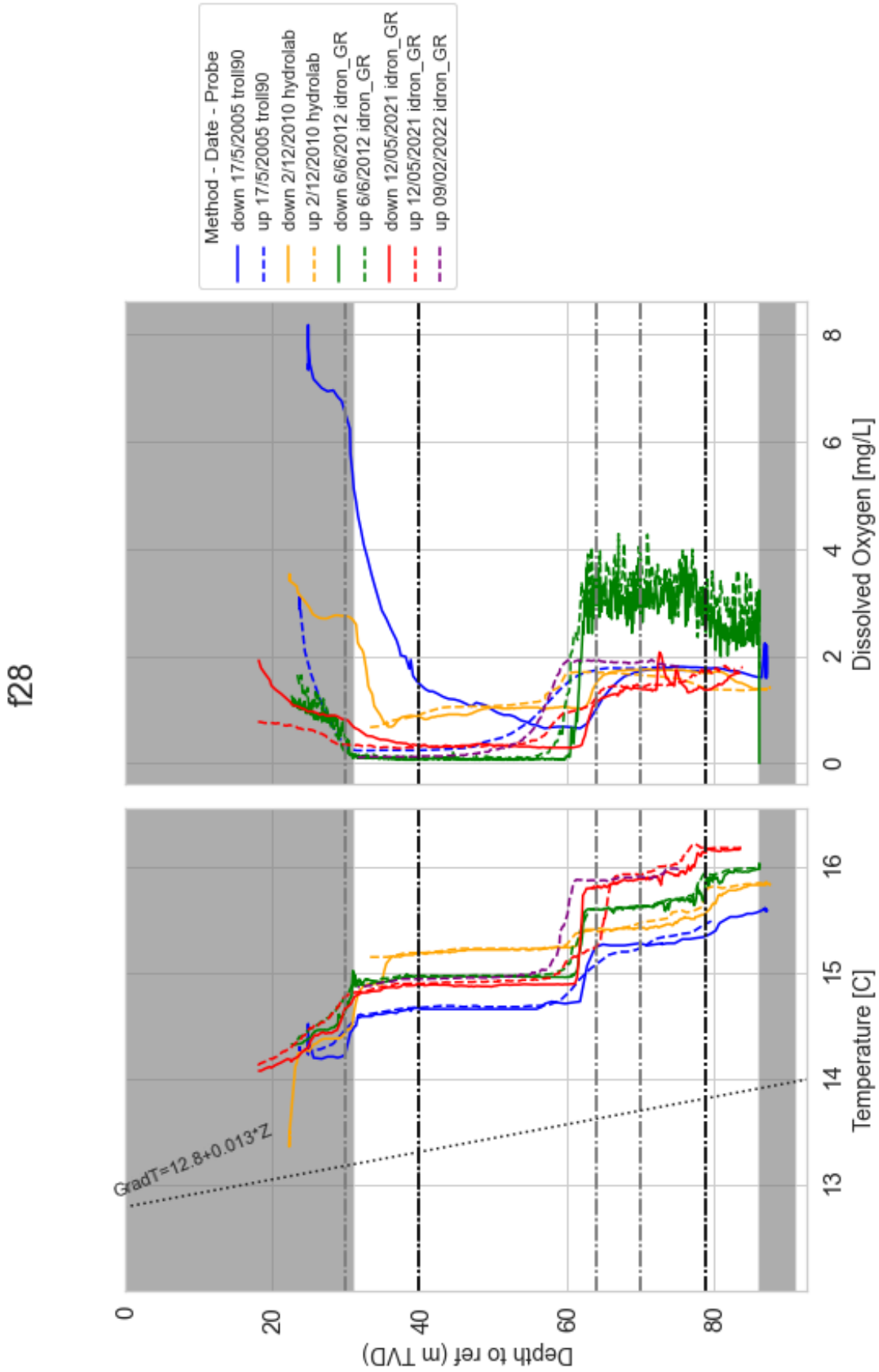
down 17/12/2010 hydrolab
up 17/12/2010 hydrolab
down 8/6/2012 idron_GR
up 8/6/2012 idron_GR
Dissolved Oxygen [mg/L]
8.2
8.4
8.6
8.8
9.0
Temperature [C]
12.0
12.5
13.0
13.5
14.0
GradT=12.8+0.013*Z
Depth to ref (m TVD)
0
10
20
30
40
50
60
70
80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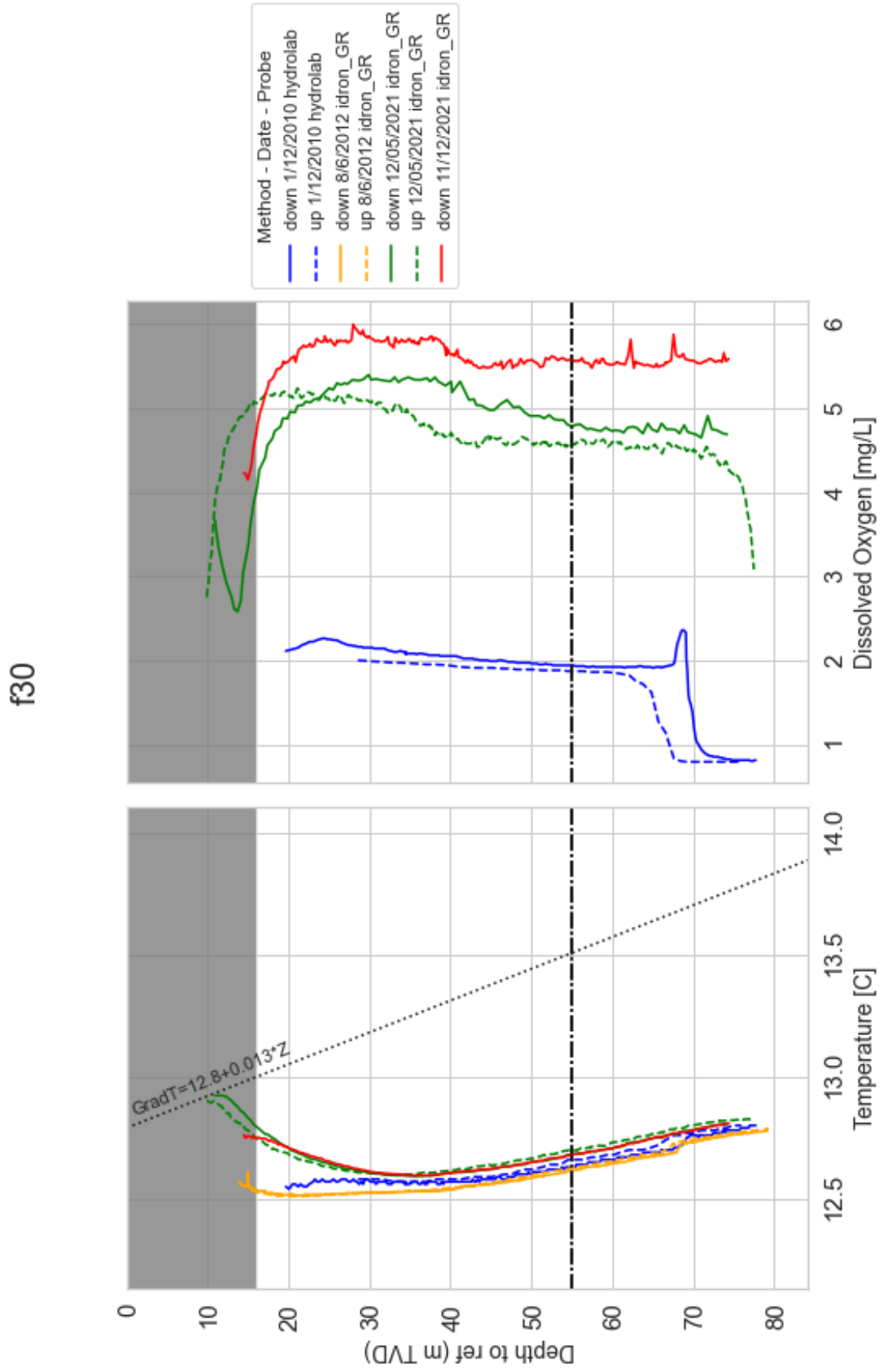
up 2/12/2010 hydrolab
down 6/6/2012 idron_GR
up 6/6/2012 idron_GR
down 12/05/2021 idron_GR
up 12/05/2021 idron_GR
up 09/02/2022 idron_GR
Dissolved Oxygen [mg/L]
0
2
4
6
8
Temperature [C]
13
14
15
16
GradT=12.8+0.013*Z
Depth to ref (m TVD)
0
20
40
60
80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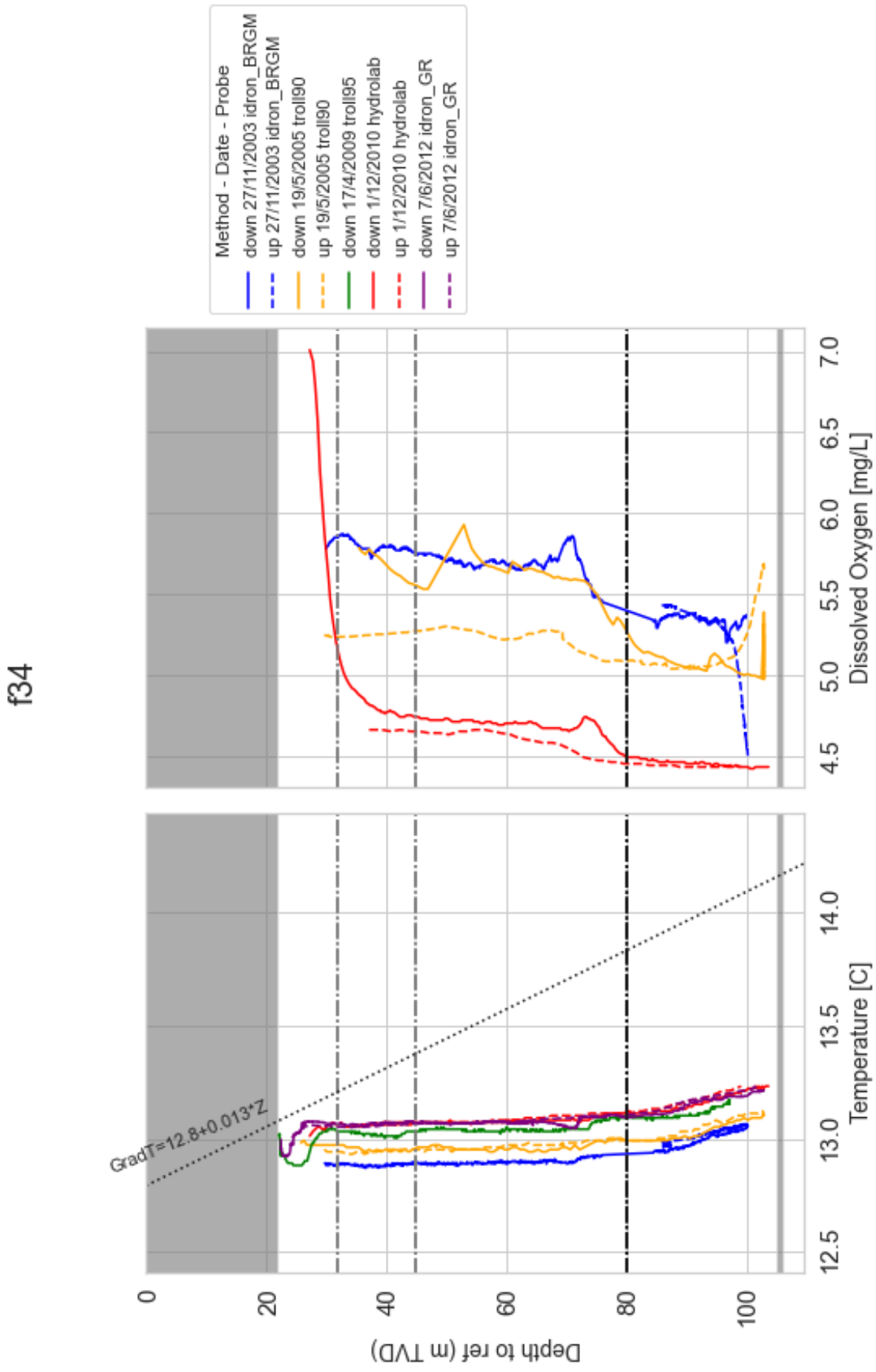
up 1/12/2010 hydrolab
down 8/6/2012 idron_GR
up 8/6/2012 idron_GR
down 12/05/2021 idron_GR
up 12/05/2021 idron_GR
down 11/12/2021 idron_GR
Dissolved Oxygen [mg/L]
Temperature [C]
GradT=12.8+0.013*Z
Depth to ref (m TVD)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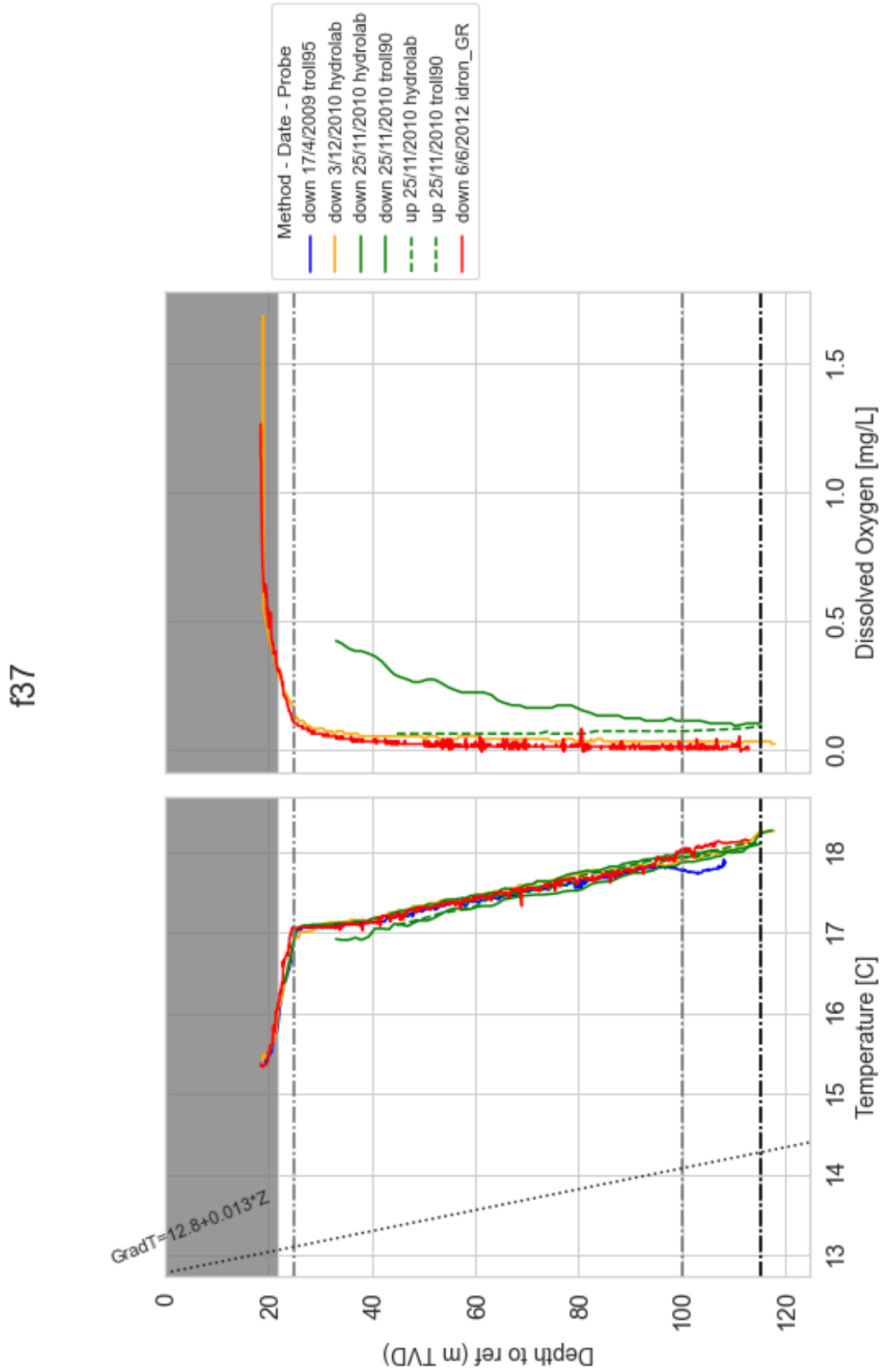
up 27/11/2003 idron_BRGM
down 19/5/2005 troll90
up 19/5/2005 troll90
down 17/4/2009 troll95
down 1/12/2010 hydrolab
up 1/12/2010 hydrolab
down 7/6/2012 idron_GR
up 7/6/2012 idron_GR
Dissolved Oxygen [mg/L]
4.5
5.0
5.5
6.0
6.5
7.0
Temperature [C]
12.5
13.0
13.5
14.0
GradT=12.8+0.013*Z
Depth to ref (m TVD)
0
20
40
60
80
100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Method - Date - Probe
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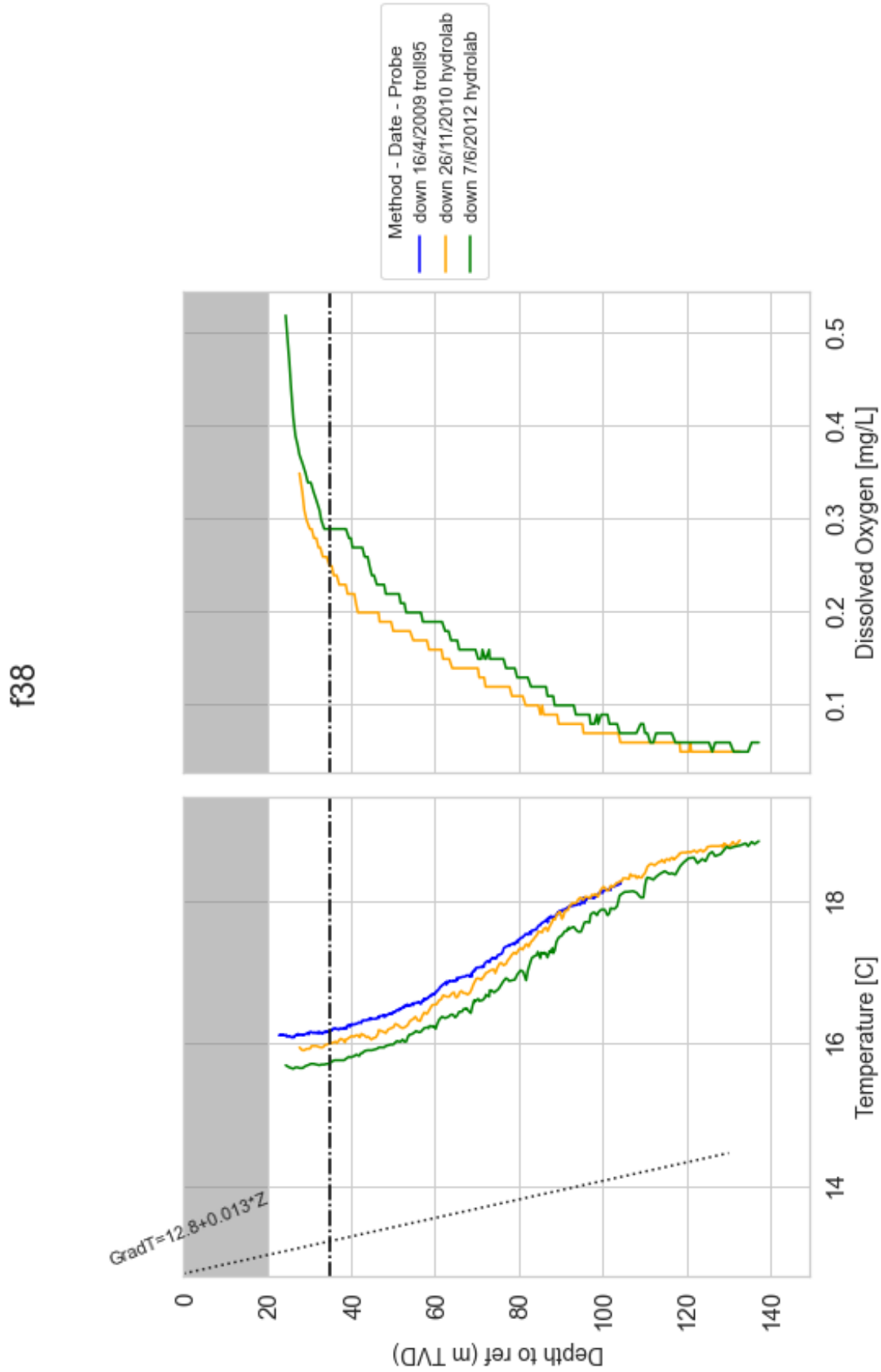
down 3/12/2010 hydrolab
down 25/11/2010 hydrolab
down 25/11/2010 troll90
up 25/11/2010 hydrolab
up 25/11/2010 troll90
down 6/6/2012 idron_GR
Dissolved Oxygen [mg/L]
0.0
0.5
1.0
1.5
Temperature [C]
13
14
15
16
17
18
GradT=12.8+0.013*Z
Depth to ref (m TVD)
0
20
40
60
80
100
120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Method - Date - Probe
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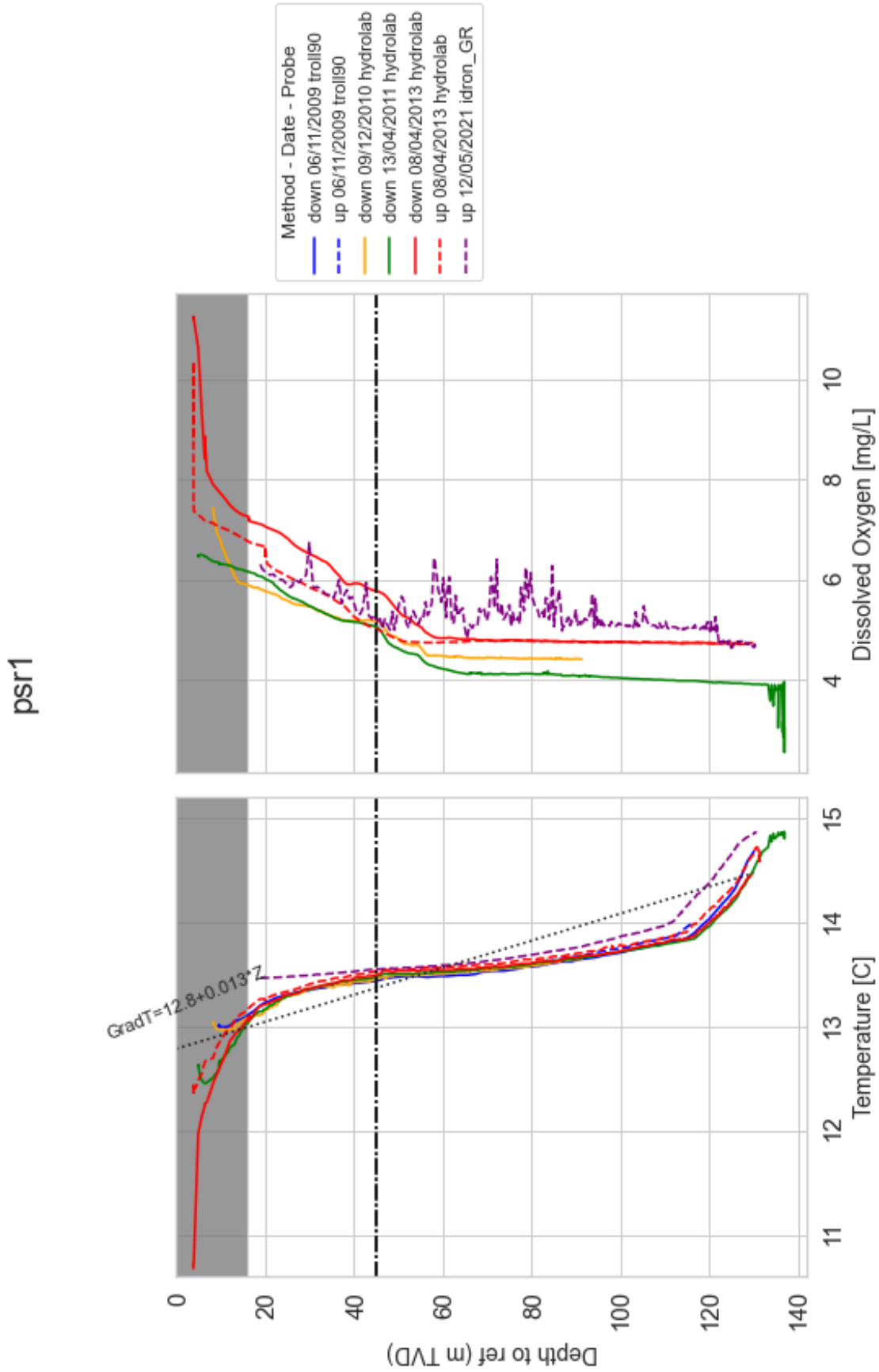
down 26/11/2010 hydrolab
down 7/6/2012 hydrolab
Dissolved Oxygen [mg/L]
0.1
0.2
0.3
0.4
0.5
Temperature [C]
14
16
18
GradT=12.8+0.013*Z
Depth to ref (m TVD)
0
20
40
60
80
100
120
140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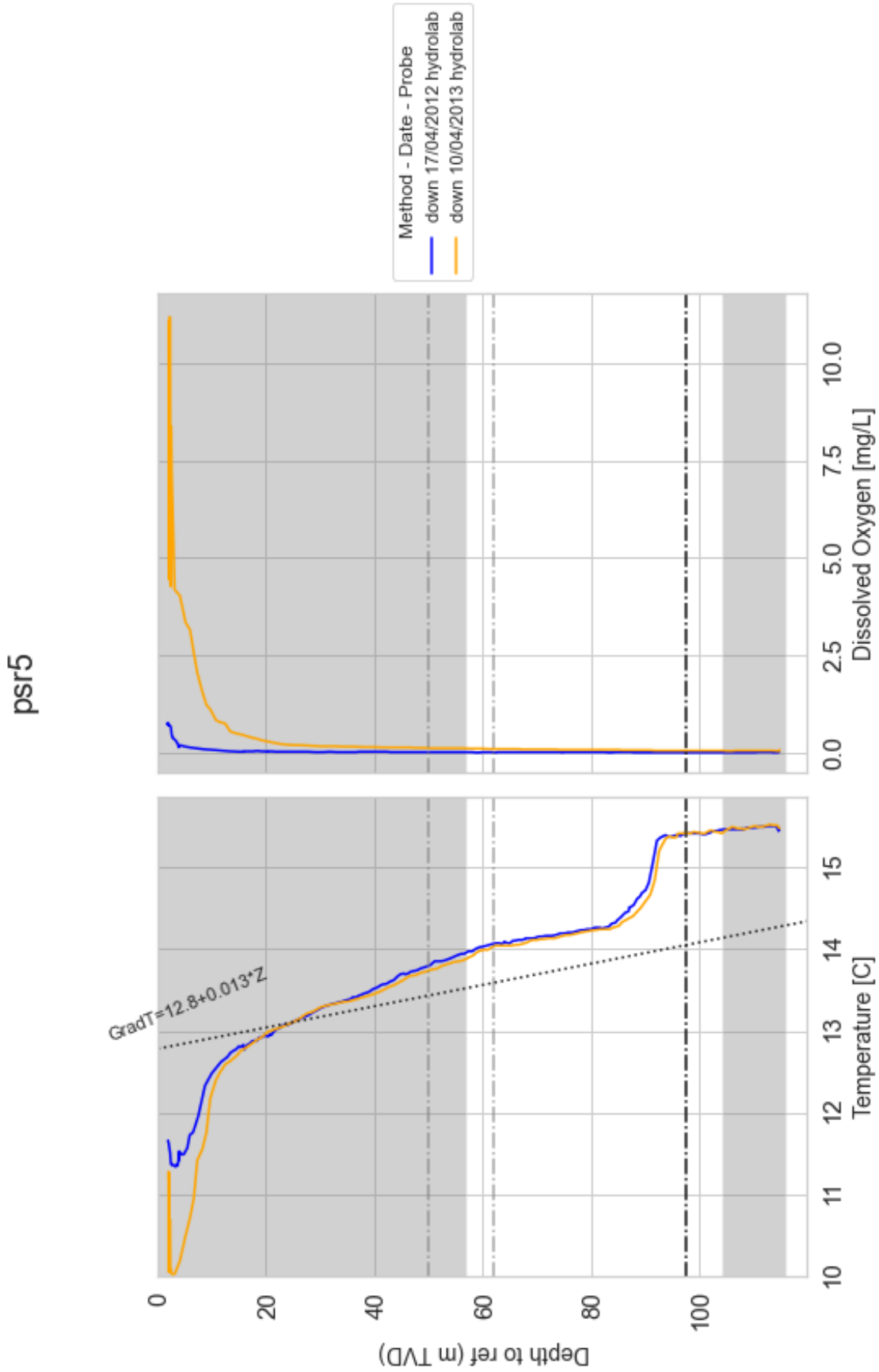
up 06/11/2009 troll90
down 09/12/2010 hydrolab
down 13/04/2011 hydrolab
down 08/04/2013 hydrolab
up 08/04/2013 hydrolab
up 12/05/2021 idron_GR
Dissolved Oxygen [mg/L]
Temperature [C]
GradT=12.8+0.013*Z
Depth to ref (m TVD)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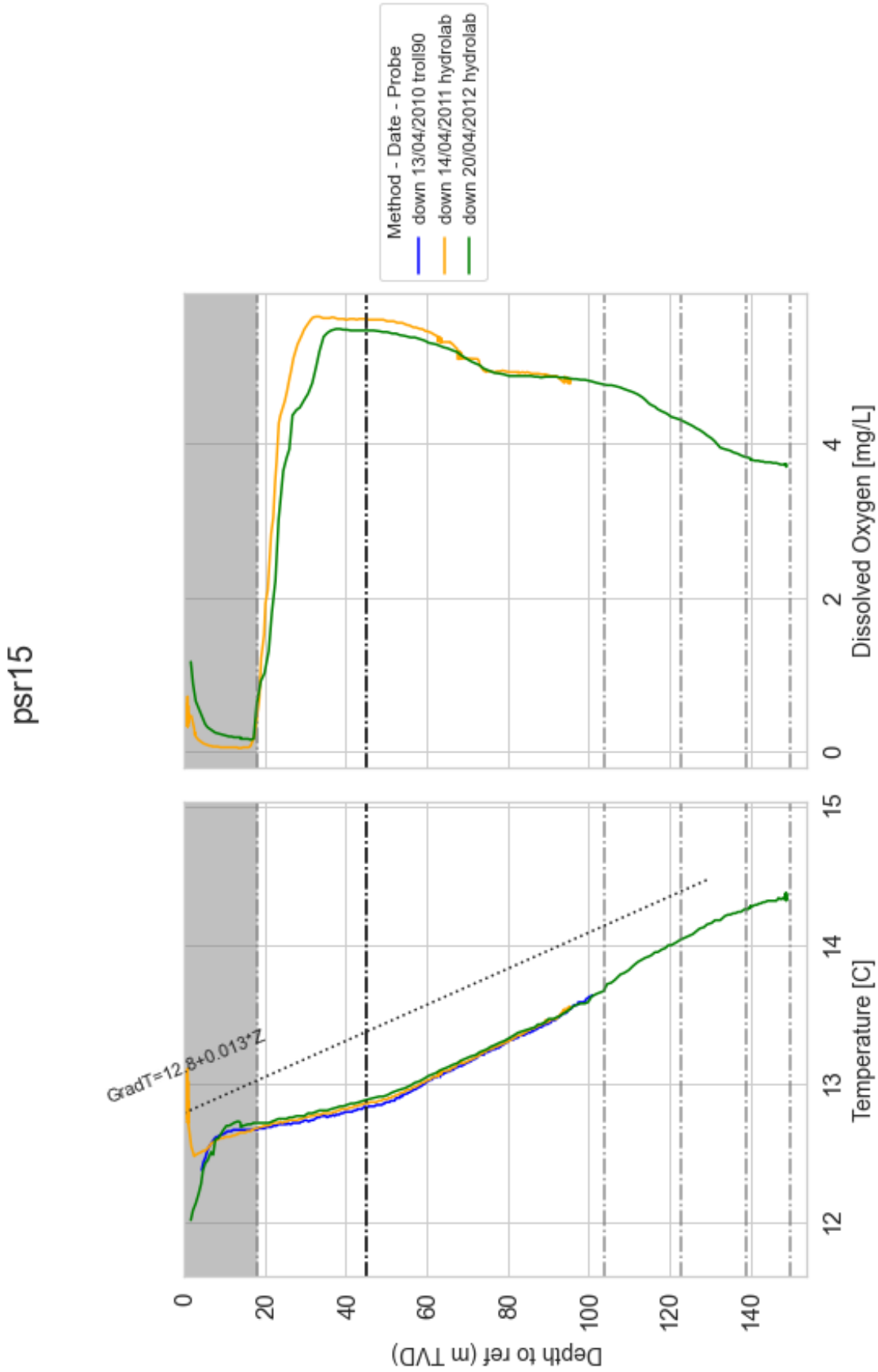
down 10/04/2013 hydrolab
Dissolved Oxygen [mg/L]
0.0
2.5
5.0
7.5
10.0
Temperature [C]
10
11
12
13
14
15
GradT=12.8+0.013*Z
Depth to ref (m TVD)
0
20
40
60
80
100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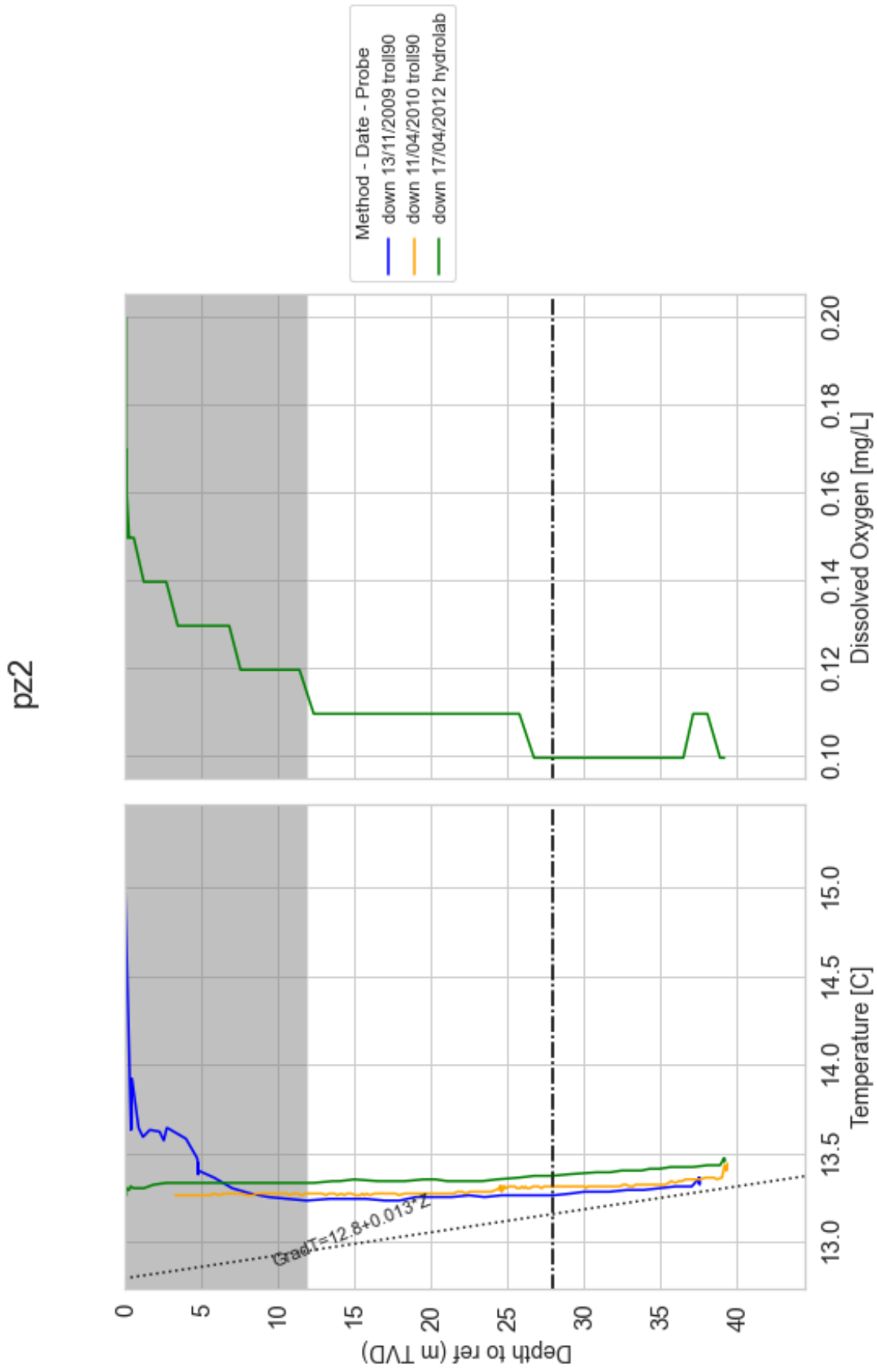
down 14/04/2011 hydrolab
down 20/04/2012 hydrolab
Dissolved Oxygen [mg/L]
0
2
4
Temperature [C]
12
13
14
15
GradT=12.8+0.013*Z
Depth to ref (m TVD)
0
20
40
60
80
100
120
140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down 17/04/2012 hydrolab
Dissolved Oxygen [mg/L]
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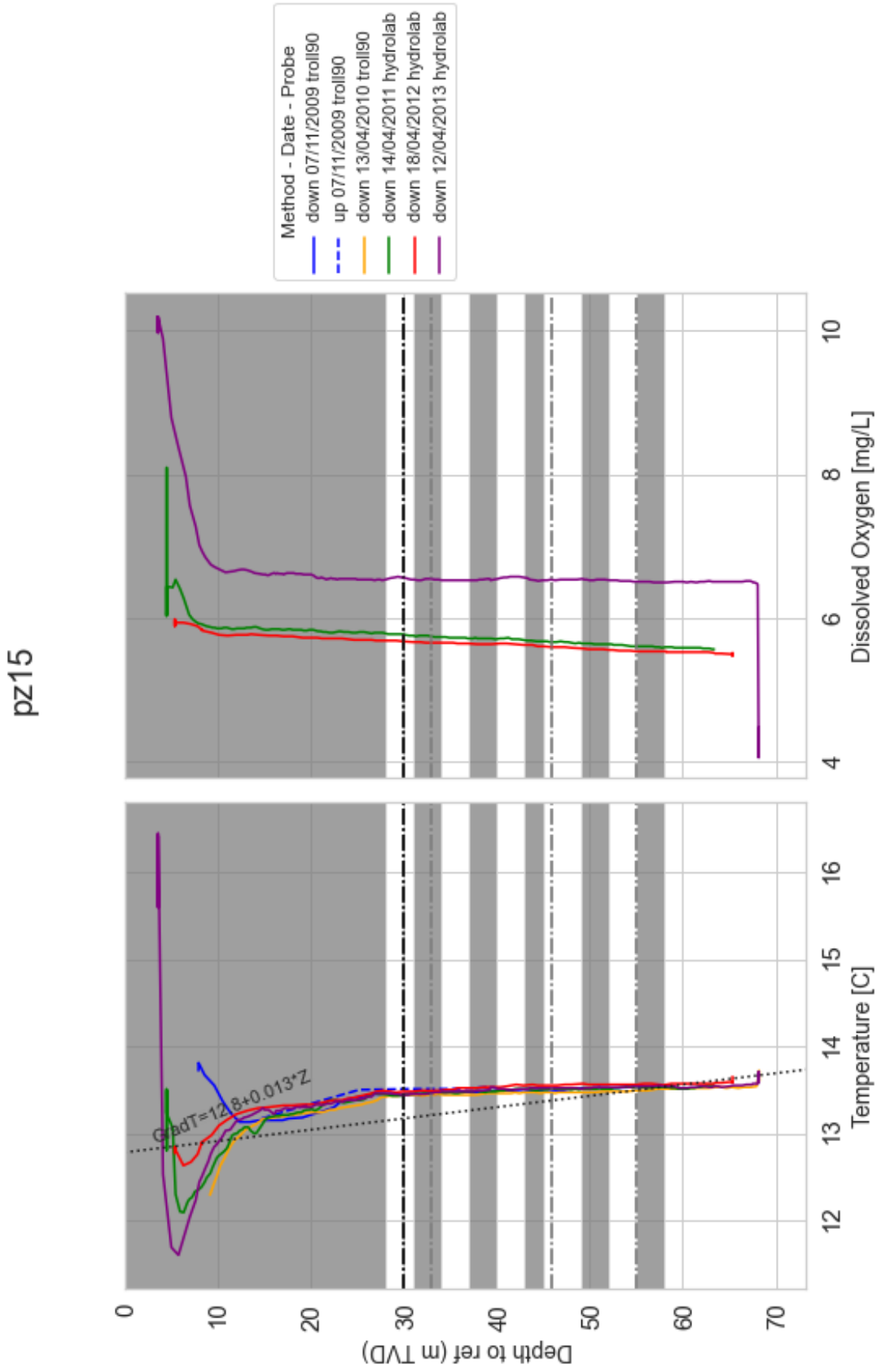
0.12
0.14
0.16
0.18
0.20
Temperature [C]
13.0
13.5
14.0
14.5
15.0
GradT=12.8+0.013*Z
Depth to ref (m TVD)
0
5
10
15
20
25
30
35
40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Method - Date - Probe
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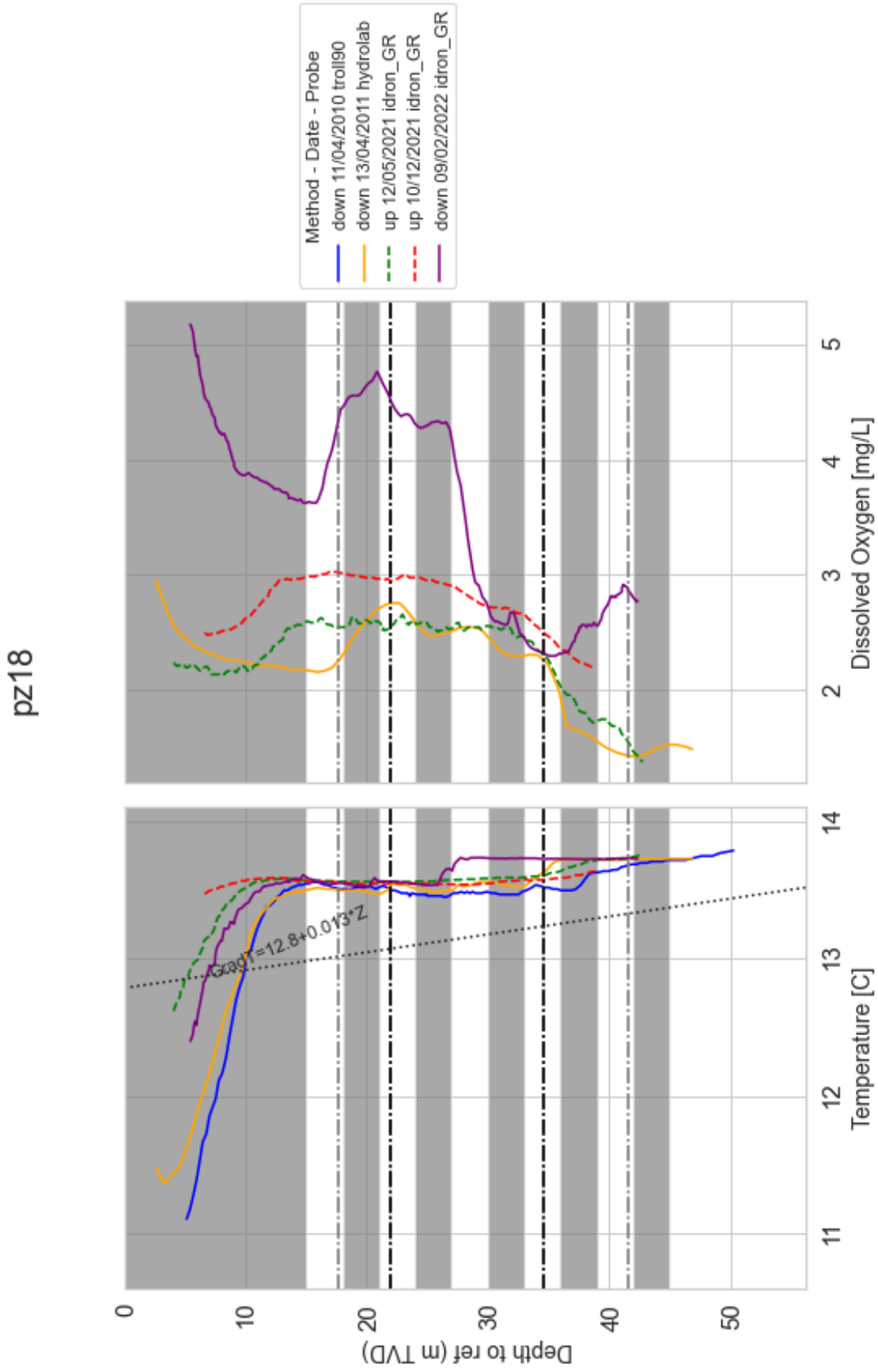
up 07/11/2009 troll90
down 13/04/2010 troll90
down 14/04/2011 hydrolab
down 18/04/2012 hydrolab
down 12/04/2013 hydrolab
Dissolved Oxygen [mg/L]
Temperature [C]
Depth to ref (m TVD)
GradT=12.8+0.013*Z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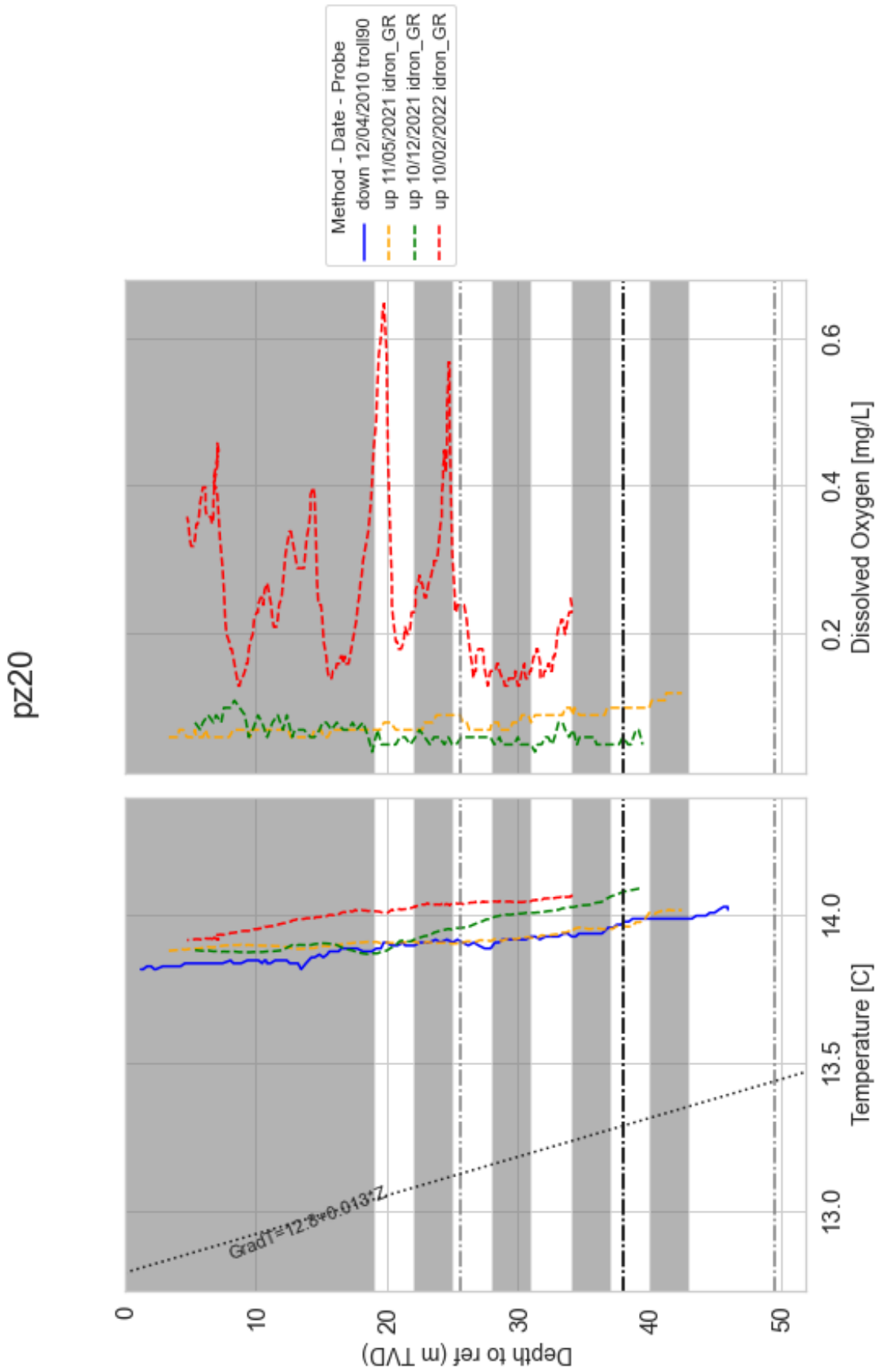
down 13/04/2011 hydrolab
up 12/05/2021 idron_GR
up 10/12/2021 idron_GR
down 09/02/2022 idron_GR
Dissolved Oxygen [mg/L]
Temperature [C]
Grad T=12.8+0.013*Z
Depth to ref (m TVD)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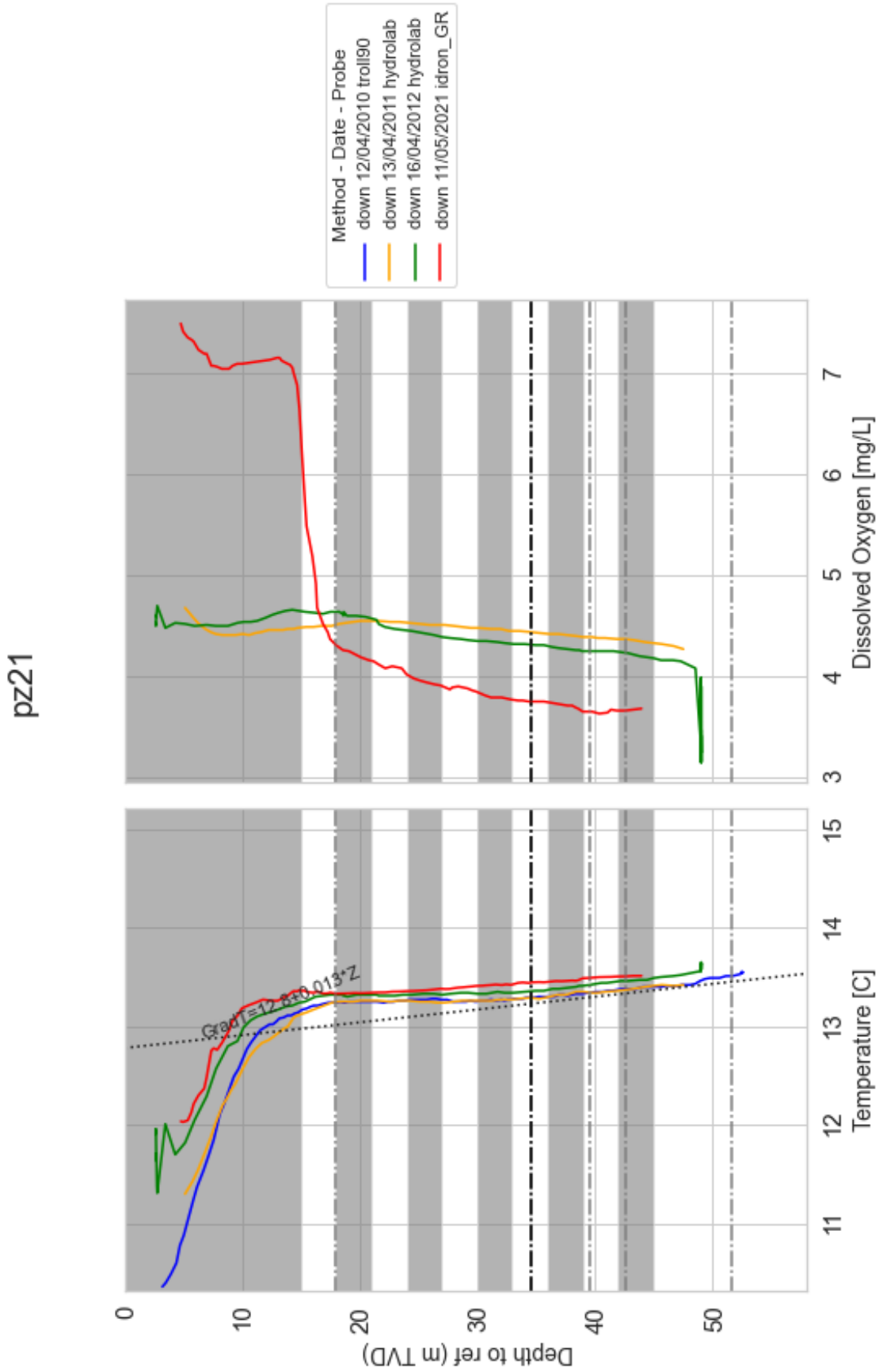
up 11/05/2021 idron_GR
up 10/12/2021 idron_GR
up 10/02/2022 idron_GR
Dissolved Oxygen [mg/L]
0.2
0.4
0.6
Temperature [C]
13.0
13.5
14.0
GradT=12.6+0.013*Z
Depth to ref (m TVD)
0
10
20
30
40
50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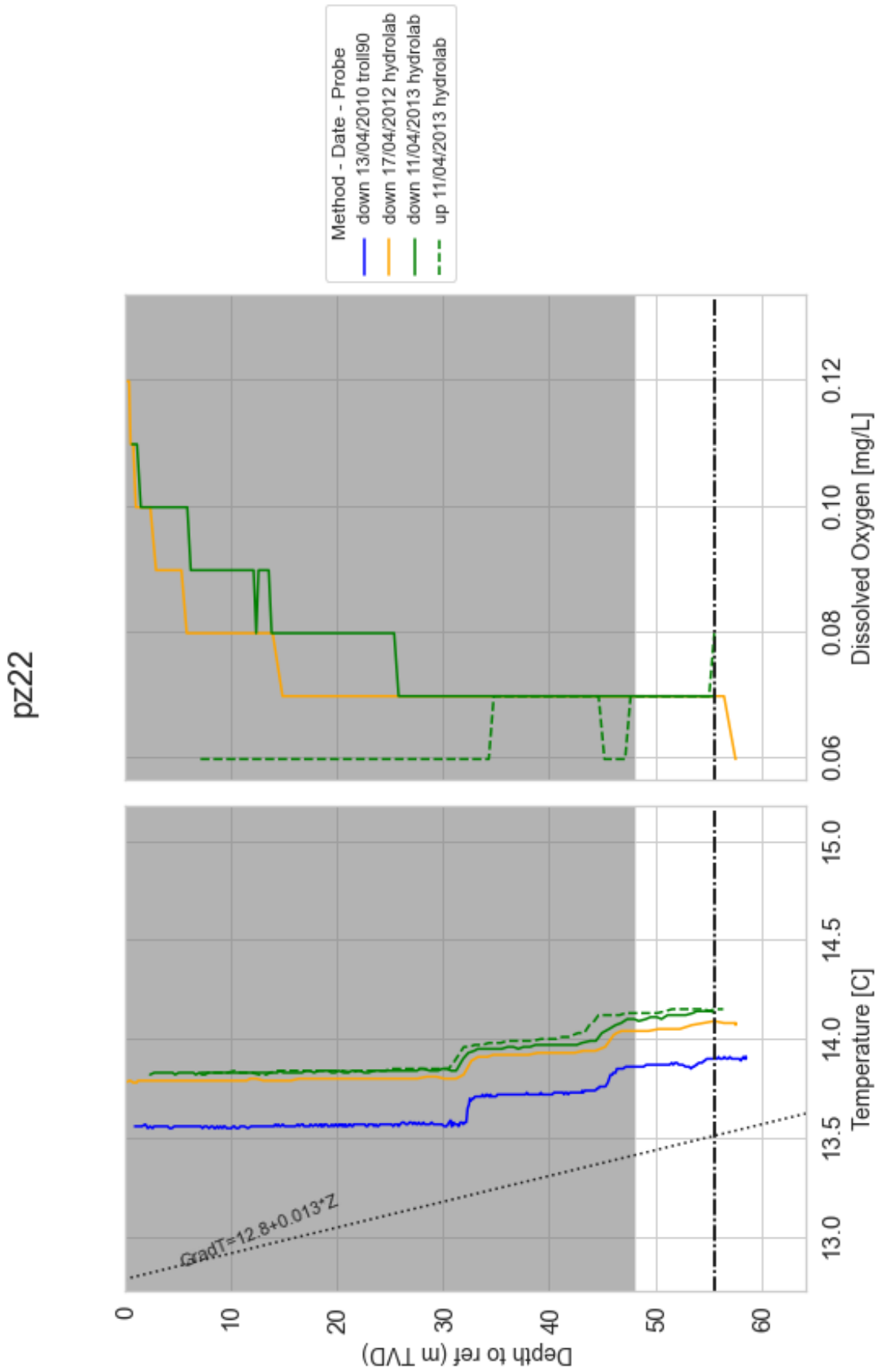
down 16/04/2012 hydrolab
down 11/05/2021 idron_GR
Dissolved Oxygen [mg/L]
Temperature [C]
Depth to ref (m TVD)
0
10
20
30
40
50
3
4
5
6
7
11
12
13
14
15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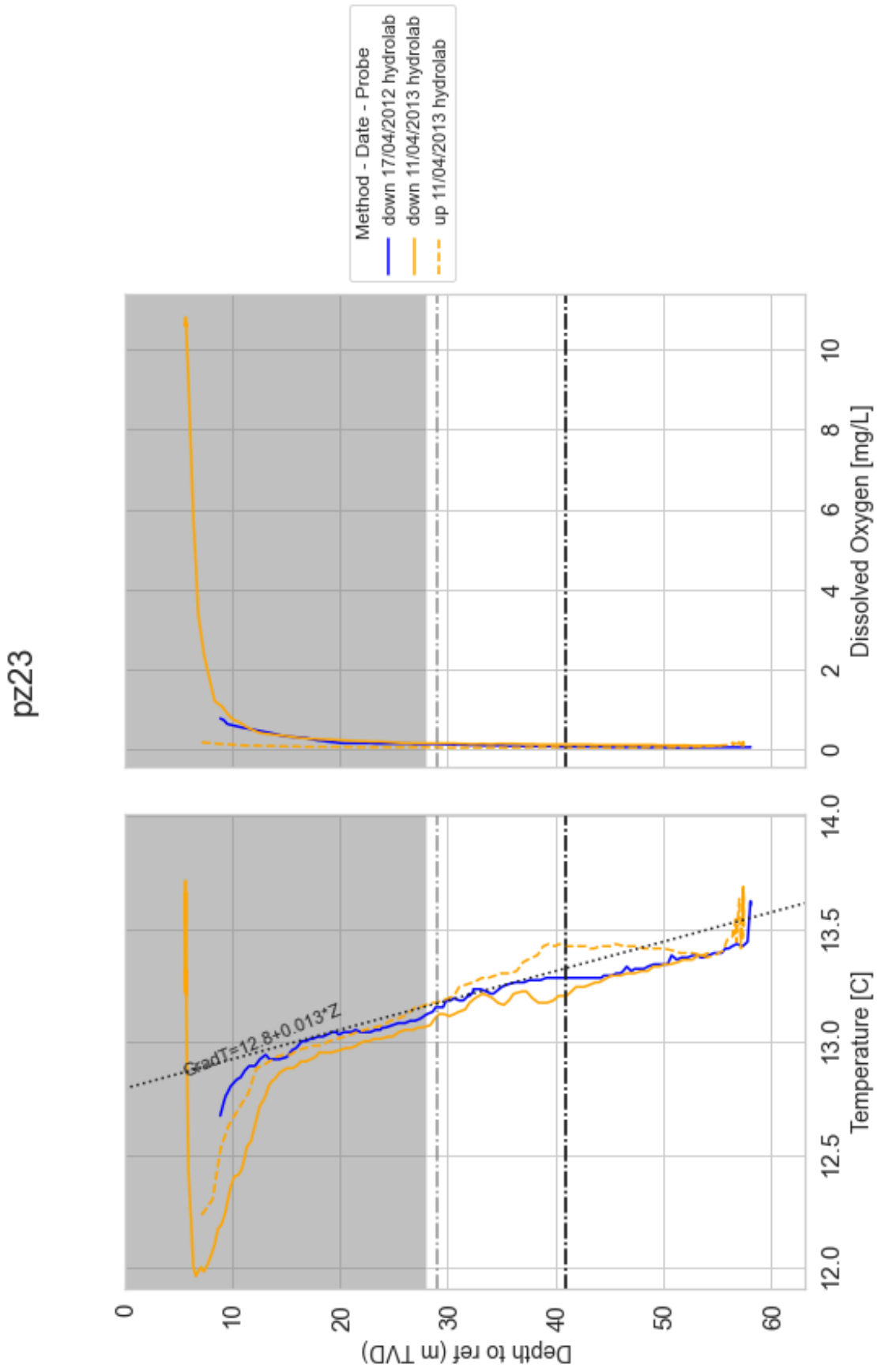
down 17/04/2012 hydrolab
down 11/04/2013 hydrolab
up 11/04/2013 hydrolab
Dissolved Oxygen [mg/L]
0.06
0.08
0.10
0.12
Temperature [C]
13.0
13.5
14.0
14.5
15.0
GradT=12.8+0.013*Z
Depth to ref (m TVD)
0
10
20
30
40
50
60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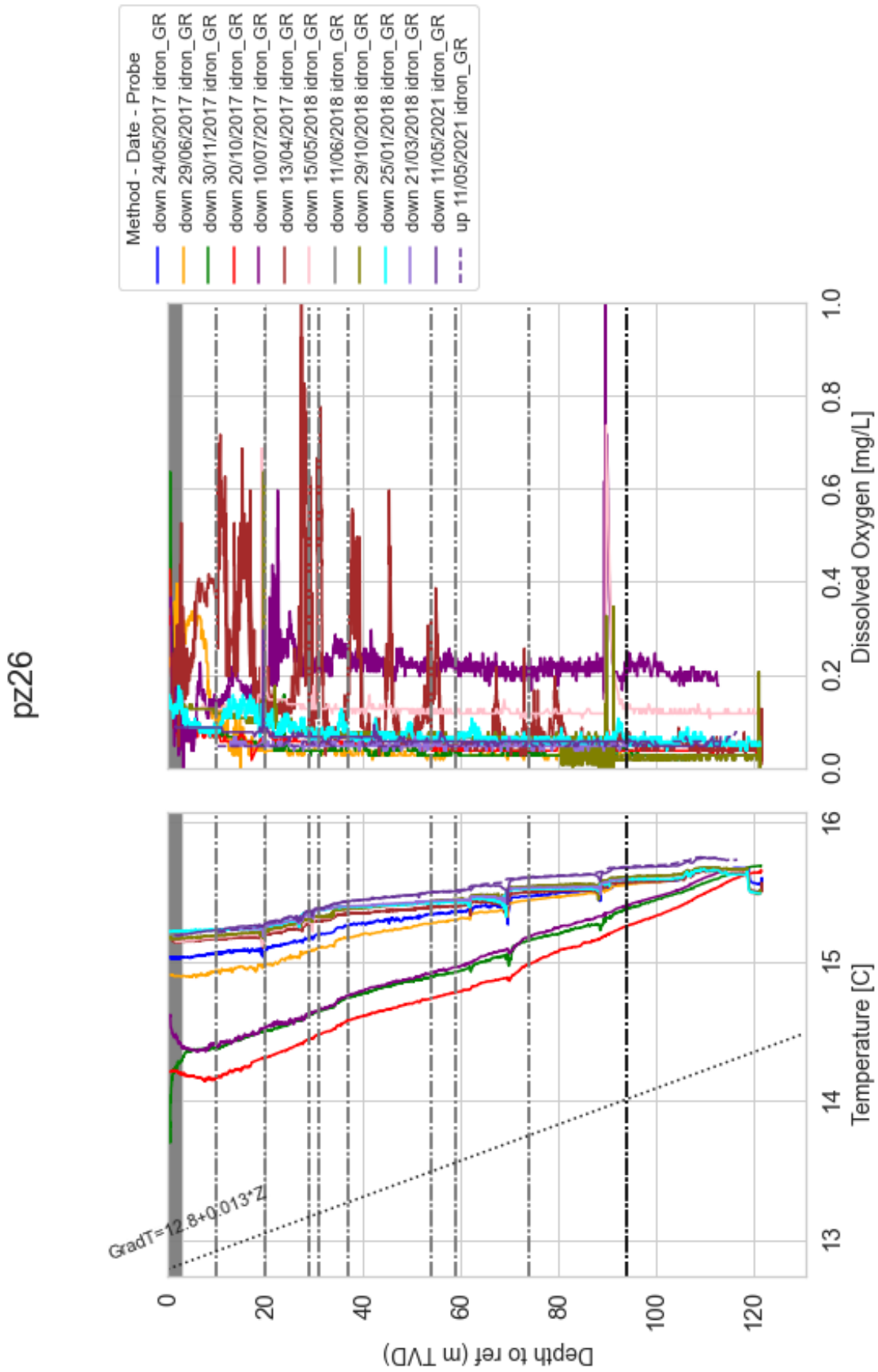
Method - Date - Probe
down 17/04/2012 hydrolab
down 11/04/2013 hydrolab
up 11/04/2013 hydrolab
Dissolved Oxygen [mg/L]
0
2
4
6
8
10
Temperature [C]
12.0
12.5
13.0
13.5
14.0
GradT=12.8+0.013*Z
Depth to ref (m TVD)
0
10
20
30
40
50
60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down 20/10/2017 idron_GR
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down 15/05/2018 idron_GR
down 11/06/2018 idron_GR
down 29/10/2018 idron_GR
down 25/01/2018 idron_GR
down 21/03/2018 idron_GR
down 11/05/2021 idron_GR
up 11/05/2021 idron_GR
Dissolved Oxygen [mg/L]
0.0
0.2
0.4
0.6
0.8
1.0
Temperature [C]
13
14
15
16
GradT=12.8+0.013*Z
Depth to ref (m TVD)
0
20
40
60
80
100
120

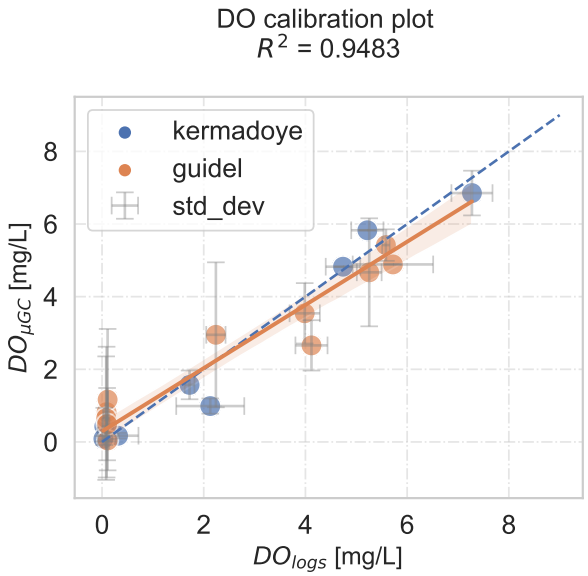

Figure 3. Calibration plot for DO measurements with the multiparameter probe (logs) vs gas chromatography (μGC) analysis made on the same samples.

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