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Abstract	Changes in the hydrologic aspects of climate are of optimum importance. However, the details of past changes in the hydrologic cycle are difficult to reconstruct. In this report we show the firs results of the analyses of paleohydrological proxies (n-alkanes) that allow the reconstruction of multiple terms of the hydrologic budget in the GPNP. We analyzed a core from Lake Trebecchi (GPNP), and after the definition of the age-dating chronology, we measured the concentrations of n-alkanes and their major indexes (ACL, Paq, C27/C31) usually selected to infer information about hydrological evolution of the ecosystems.
Keywords	Hydrology, chemical biomarker, environmental changes

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1 Executive summary

Task 5.2, lead by CNR, will provide data about the historic evolution of the ecosystems for selected sites in the Gran Paradise National Park.

The study of past climatic change and of the multiple interactions between geosphere, hydrosphere and biosphere require a holistic approach to better understand these complex and often non-linear relationships. In paleoclimatic studies, every discipline aims to develop its own method to reconstruct past climate variability choosing different proxies. However, the strongest approach in climatic reconstructions is to combine evidence from different type of proxy in a multi-proxy study. The choice of proxies for such studies is of primary importance. They should provide sensitive climatic indicators and be complementary in their ability to reconstruct climate. Each proxy can provide us with information about one or more climate-related environmental processes. Through a multi-proxy approach, we can therefore obtain information regarding different aspects of the whole environmental, climatic and ecological system.

In environmental reconstructions, the major advantage of the multi-proxy approach resides in the unique opportunity of obtaining independent lines of evidence. Every proxy has its own strengths and weaknesses, but by identifying consistencies, weaknesses, agreements and disagreements among proxies, it is possible to achieve a more reliable paleoclimatic reconstruction. A multi-proxy paleoclimatic reconstruction starts with the collection of the existing climatic data present on the sampling area: instrumental observations of the weather parameters can thereby be correlated with experimental proxy results, in order to produce a detailed record of climate changes. Instrumental data are of primary importance but, even in the best-case scenario, they span for no more than a few decades. Where instrumental observations are lacking, information on the climate can sometimes be obtained from the analysis of historical records. Information from historical documents must be converted into numeric records based on specific indicators. In a second step, these indicators must be related to climatic parameters (e.g., rainfall, temperature, etc.) in order to obtain a reliable climatic record. Where neither instrumental observations nor historical records are available, we can only rely on indirect measurements (proxy-data) of climate change through a multidisciplinary approach that includes the analysis of the distribution of fossil organic and inorganic compounds. And this is the case of Gran Paradise National Park (GPNP), thus we started this study trying to measure different climate related proxies, in order to retrieve information about the major environmental and land use changes that characterized the GPNP in the last 150-200 years.

In an ideal environment, the historical record of atmospheric deposition should be perfectly recorded, and the relationship depth/age continuous and preserved. Moreover, non-significant post-depositional physical or chemical transformations which can alter or remobilize the element of interest should be present. According to this definition of ideal environment, tree rings, oceanic corals, lake and marine sediments, ice cores from mountainous glaciers and polar ice caps, and peat cores from ombrotrophic bogs are the most useful matrices for paleo-environmental and paleoclimatic reconstructions. That’s the reason because we starting analyzing sediment form lakes in GPNP.

The first information about the main environmental changes that characterized GPNP during the last 150-200 years is arising through physical and geochemical analyses that are going to carry out on samples collected from sediment records of Lake Trebecchi, located in Gran Paradise National Park (45° 30’ 07’’ N, 07° 08’ 40’’ E).

Several activities are planned and are going on. The sampling activities were carried out in October 2016, during which the CNR researchers have retrieved 2 cores from the sediment of Lake Trebecchi. Physical and geochemical analyses, which comprehend the determination of several parameters such as bulk density, organic matter content, major and trace elements, and C-N isotopes ratios will be carried out.

At now the CNR team obtained data about chronology and n-alkanes and all the data are reported in the dataset and described in this report.

2 Purpose

Changes in temperature and hydrology can have a significant impact on both terrestrial and aquatic ecosystems. Understanding the hydrological evolution and producing quantitative estimates of hydrological variables (i.e. precipitation, relative humidity, or temperature) may lead to a better understanding of regional climatic changes and hydroclimatic variability. In this context, n-alkanes have been gaining increasing concern in biogeochemical studies for past global change (Rao et al., 2008), since they are chemically stable, resistant to diagenesis and have naturally high content in sediments. In particular, compound-specific hydrogen isotope ratio (δD) analysis has emerged as a powerful tool to track local to regional paleo-hydrological changes (e.g. Schefuß et al., 2011), since the δD values of organic biomarker molecules have been shown to be directly related to δD values of meteoric water available to the biomarker source organisms (Sachse et al., 2012). Furthermore, the molecular distribution of n-alkanes can be used to differentiate the corresponding biological sources: long-chain molecules (with 25 to 33 carbon atoms) are mainly produced by terrestrial plants (Eglinton and Hamilton, 1967; Rieley et al., 1991). Middle-molecular-weight n-alkanes are mainly produced by submerged/floating aquatic macrophytes (Ficken et al., 2000; Viso et al., 1993) whilst the short-chained n-alkanes are constituents of the membranes of algae and bacteria (Cranwell et al., 1987; Han and Calvin, 1969).

Lakes accumulate sediments continually, a process that has been on-going since their formation, in many cases for several thousand years or even longer. The sediment consists of biological remains from the lake itself and its surroundings, as well as soil particles and other non-biological material originating from the lake catchment and also the atmosphere. Hence, the sediment sequence in each lake is a continuous environmental archive, which contains information about the history of the lake and its surroundings. Hence, lake sediment records are one of the best archives for obtaining high-resolution records (Brauer et al., 2008).

Lake Trebecchi, located in Gran Paradise National Park (45° 30’ 07’’ N, 07° 08’ 40’’ E) belongs to the catchments of the Dora of Savarenche stream. The lake is not affected by hydro-morphological alterations, and is located above the local timberline with their watershed belonging to the Alpine and nival altitudinal zone. Lake Trebecchi fills a shallow depression produced by glacier erosion; its free surface altitude is 2729 m, with a maximum depth of 7.5 m.

The aim of these first set of analyses is to produce an high-resolution hydrological datasets analysing sediments of Lake Trebecchi in order to: i) provide a quantitative paleo-hydrological reconstructions of the last 200 years from a terrestrial archive; and ii) correlate this terrestrial record with different proxy records in the same core.

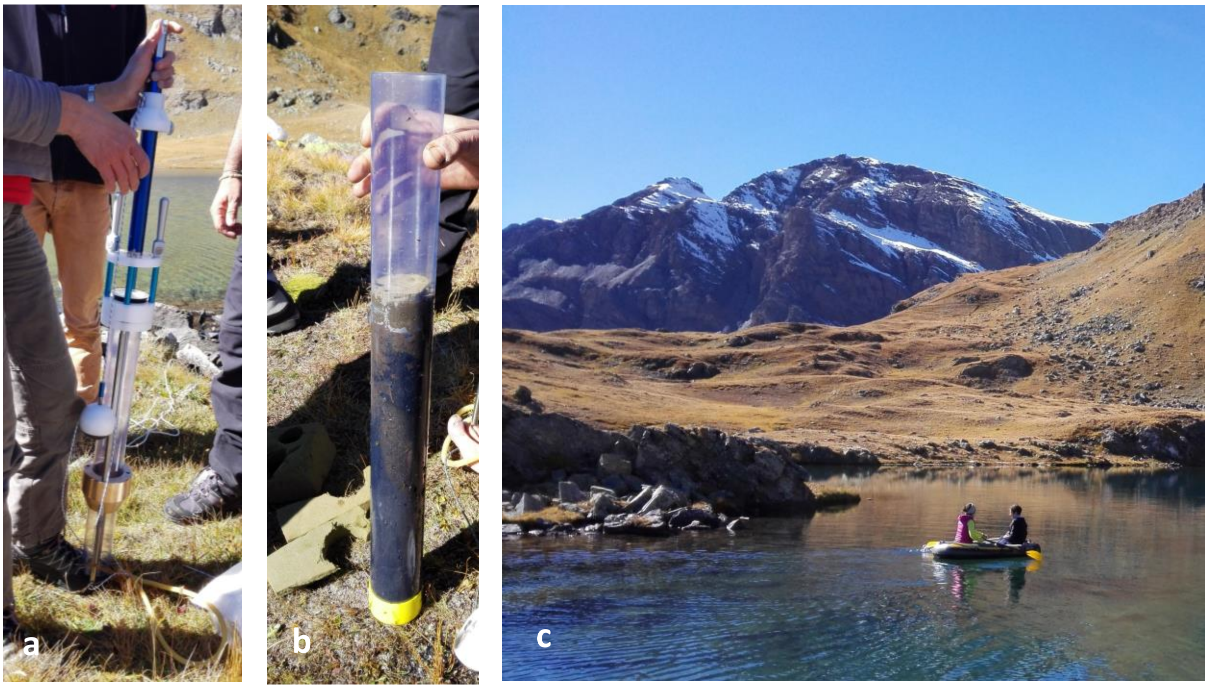
3 Description of the work carried out

3.1 Coring, Sampling and subsampling

On October 2016 we sampled sediments form Lake Trebecchi retrieving 2 cores approximately 30 centimetres long. The field strategy involved collecting short cores from the deepest point of the lake previously indicated by the bathymetry studied by Tiberti et al (2013). Sediment cores were taken using a gravity corer equipped with a percussion system to improve penetration. Coring was done from a rubber boat (Figure 1). Immediately after retrieval, cores were transported to the lakeshore, and then transported to the laboratory at the CNR-IDPA for further analyses.

In the CNR-IDPA laboratory the first core was cut into 1-cm slices and each slice was then sub-sampled for physical and chemical analyses. The other core was conserved as archive at 4-5°C.

Figure 1. Sediment corer (a), one of the 2 cores retrieved with the corer (b), sampling time on the rubber boat (c).



3.2 Dating

In order to extract climate-related information from lake sediments, it is essential to establish a reliable chronology. Some lakes have annually laminated sediments, also called varves, where couplets of light and dark bands are formed each year similar to tree-rings, which allow good chronological control by simply counting dark and light layers. However, most often the sedimentary records are homogenous and without any pronounced annual layers, requiring different dating techniques. This is also the case of Lake Trebecchi. Commonly applied dating methods are based on radio-isotopic dating, such as lead (Pb-210, half life 22.3 yrs) and carbon (C-14, half-life >5500 yrs). Due to the half-life of these isotopes, the lead method can be applied for sediments that are not older than 150-200 years, whereas the carbon method is applicable for sediments up to several tens of thousand years old.

3.3 Chemical Analysis

Sediment samples were freeze-dried and ground prior to extraction. Soluble organic matter was extracted 2 times with a solvent mixture of dichloromethane-DCM: methanol-MeOH (9:1, v/v), using an Accelerated Solvent Extractor (ASE) at 100°C and 1500 psi for 15 min in 3 cycles. For the extraction, a subset of 2-3 g of the samples was used. Each total extract was evaporated to near dryness under a N_2 flow, dissolved in DCM and, depending on the n-alkanes content, 10-50 µg of internal standard (5-α-androstane) was added. The total extracts were separated by passing them over chromatographic glass columns (ca. 20 cm height, ø2.5 cm) filled with ca. 25 cm^3 activated silica gel (0.040–0.063 mesh) into 3 fractions:

- F1: Hydrocarbons were eluted with hexane,
- F2: Apolar compounds with a mixture of hexane:DCM (1:1, v/v),
- F3: Polar compounds, including glycerol diethers and glycerol dialkyl glycerol tetraethers, with DCM:MeOH (1:1, v/v)

The F1 components were identified and quantified via gas chromatography mass spectrometry with a 6,890-N GC system coupled to a quadrupole mass spectrometer 5973 (Agilent Technologies). Separation was achieved on a HP-5MS column (30 m×0.25mm; film thickness 0.25 µm). An external n-alkanes standard mixture (n-C_{10} to n-C_{40}) was used as the reference material and the components was analysed daily with the same procedure of samples. The carbon numbers of the extracted n-alkanes were determined by comparison with the retention times of the external standard mixture, and then the relative abundances of the extracted n-alkanes homologues were determined by comparing their peak areas with the peak area of the internal standard (5-α-androstane).

F2 and F3 fractions were conserved for future analyses and stored at -20°C. F2 will be useful to assess the presence of alcohols and F3 for the analyses of GDGT (glycerol dialkyl glycerol tetraethers).

3.4 Quality assurance and control

Several laboratory blanks were processed together with samples: extraction ASE cells were filled with diatomaceous earth and spiked with known amounts of internal standard solutions of 5α-androstane. The quantification was performed through the isotope dilution technique and absolute quantities of each compound were corrected by the individual response factor, obtained by repeated injections of a solution containing all native and internal standard compounds. Results were finally corrected by the mean blank plus 3 times the standard deviation.

To avoid any source of contamination from the laboratory equipment, all glassware, diatomaceous earth, silica gel and filters were heated at 400 °C for 24 h in the muffle furnace. Extraction cells and other stainless steel tools were cleaned in the ultrasonic bath with convenient solvents before use.

4 Preliminary results and discussions

4.1 Age dating - Chronology

To determine ^{210}Pb activities, the measurement of its daughter nuclide ^{210}Po was accomplished via alpha spectrometry according to Frignani and Langone (1991).

^{209}Po was used as an internal standard for calculation of the efficiency. The two isotopes (^{210}Po and ^{209}Po) were alpha-counted with a silicon barrier detector coupled with a multichannel analyzer.

Excess ^{210}Pb (^{210}Pbex) was calculated from the difference between total and supported ^{210}Pb. The value of supported ^{210}Pb activity was assumed constant along the core and estimated from the values of the deepest sediment levels, where ^{210}Pb was assumed to be in radioactive equilibrium with its parent ^{226}Ra.

Sediment accumulation rates and the age of sediments were calculated by using a constant flux–constant sedimentation assumption for the portion of the log-normal profile of ^{210}Pb activity vs. sediment depth, below the surface.

The core was dated measuring the activity of ^{210}Pb at the CNR ISMAR. Dried samples were analysed with a resolution of 2 cm in the first 10 cm of the core, and every 4 cm in the last part.

Table 1. Total ^{210}Pb activity as measured along the entire core.

Sample depth (cm)	^{210}Pb activity (Bq/Kg)	Age	Chronology
0	1167,5 ± 28,4	4,2	2013
2	1036,6 ± 31,6	21,2	1996
4	163,5 ± 5,3	38,2	1979
6	198,3 ± 7,6	55,2	1962
8	40,8 ± 1,9	72,2	1945
10	62,2 ± 2,9	89,2	1928
14	36,1 ± 2,1	123,2	1894
18	20,3 ± 0,9	157,2	1860
22	7,1 ± 0,4	191,2	1826
26	8,4 ± 0,4	225,1	1792
30	5,5 ± 0,4	259,1	1758

4.2 Chemical analyses

The Table 2 and Figure 2 show the variation of total extracted n-alkanes, ALC, C_{27}/C_{31} ratio and Paq index along the entire core.

Carbon numbers of extracted n-alkanes for most samples ranged from n-C21 to n-C35 (Dataset).

The total concentration of extractable n-alkanes ranges from 10.2 to 156.36 µg/g. All samples show a predominance of long-chain n-alkanes, indicating a terrestrial origin.

The total concentration of extractable n-alkanes shows a relatively high concentration in the first 10 cm of the core and after it decreases, with some oscillations, until 30 cm.

The ACL (average chain length, ratio below) is a method applied to study the source of n-alkanes in environment based on the concentration of the odd-carbon-n-numbers of the n-alkanes of higher plants. The fundamental assumption for using ACL as such a proxy is that leaf lipids derived from grasslands may on average have longer chain lengths than leaf lipids from plants in forests. Moreover in warmer climates, plants produce longer chain of n-alkanes. Little environmental changes occurring in a system are characterized by constant values of ACL.

$$ACL_{25-33} = \frac{\Sigma_{odd} C_n * n}{\Sigma_{odd} C_n}$$

Samples from Lake Trebecchi have the ACL quite constant at high values along the entire core (26,9 ± 1,08), suggesting that no important environmental changes have been in the lake during the last 200 years.

Ratios of n-alkanes of different chain lengths have been used as indicators of the relative contributions of aquatic to terrestrial plants to sediments, particularly in lacustrine systems. Submerged vascular macrophytes are characterized by medium chain length n-alkanes. Their abundance relative to terrestrial plants (characterized by long chain n-alkanes) has been quantified by the ''P- aqueous (P_{aq})''. The P_{aq} ratio (below) compares the abundance of medium chain to the sum of the abundance of medium and long chain n-alkanes.

$$Paq = \frac{(C_{23} + C_{25})}{(C_{23} + C_{25} + C_{29} + C_{31})}$$

Emergent aquatic plants have a distribution pattern midway between those of non-emergent and terrestrial plants (Ficken et al., 2000). For the modern plants, this proxy gives average values of 0.09 for terrestrial (range 0.01±0.23), 0.25 for emergent (range 0.07±0.61) and 0.69 for submerged/ floating species (range 0.48±0.94) (Ficken et al., 2000). The obtained data suggest an influence from emergent and submerged/floating species, as it’s confirmed also by the C_{27}/C_{31} ratio.

Table 2. n-Alkanes distribution in the core samples: Total n-Alkanes concentration, average chain length (ACL), Paq, C_{27}/C_{31} ratio

Sample	Core Depth (cm)	Total n-alkanes (µg/g)	ACL[b]	Paq[c]	C_{27}/C_{31}
0-1	0-1	118,31	25,5	0,82	3,40
1-2	1-2	156,36	27,3	0,64	1,41
3-4	3-4	96,07	25,6	0,52	2,61
6-7	6-7	127,27	25,8	0,46	4,78
8-9	8-9	59,26	27,5	0,59	2,03
10-11	10-11	38,60	26,3	0,85	2,96
11-12	11-12	61,91	26,2	0,85	2,26
12-13	12-13	96,36	25,9	0,89	2,47
13-14	13-14	130,69	25,7	0,91	2,47
14-15	14-15	143,37	25,4	0,95	2,63
17-18	17-18	85,97	26,9	0,64	1,38
18-19	18-19	91,78	26,5	0,74	1,78
19-20	19-20	142,59	26,4	0,74	2,26
20-21	20-21	75,93	26,8	0,74	1,21
21-22	21-22	28,72	26,9	0,72	2,14
22-23	22-23	21,06	28,6	0,35	1,04
24-25	24-25	55,96	27,4	0,62	2,54
25-26	25-26	36,40	27,1	0,69	2,54
26-27	26-27	34,65	28,1	0,52	1,31
27-28	27-28	10,12	29,2	0,24	0,93
28-29	28-29	14,98	28,1	0,42	1,48
29-30	29-30	12,11	28,2	0,48	1,44

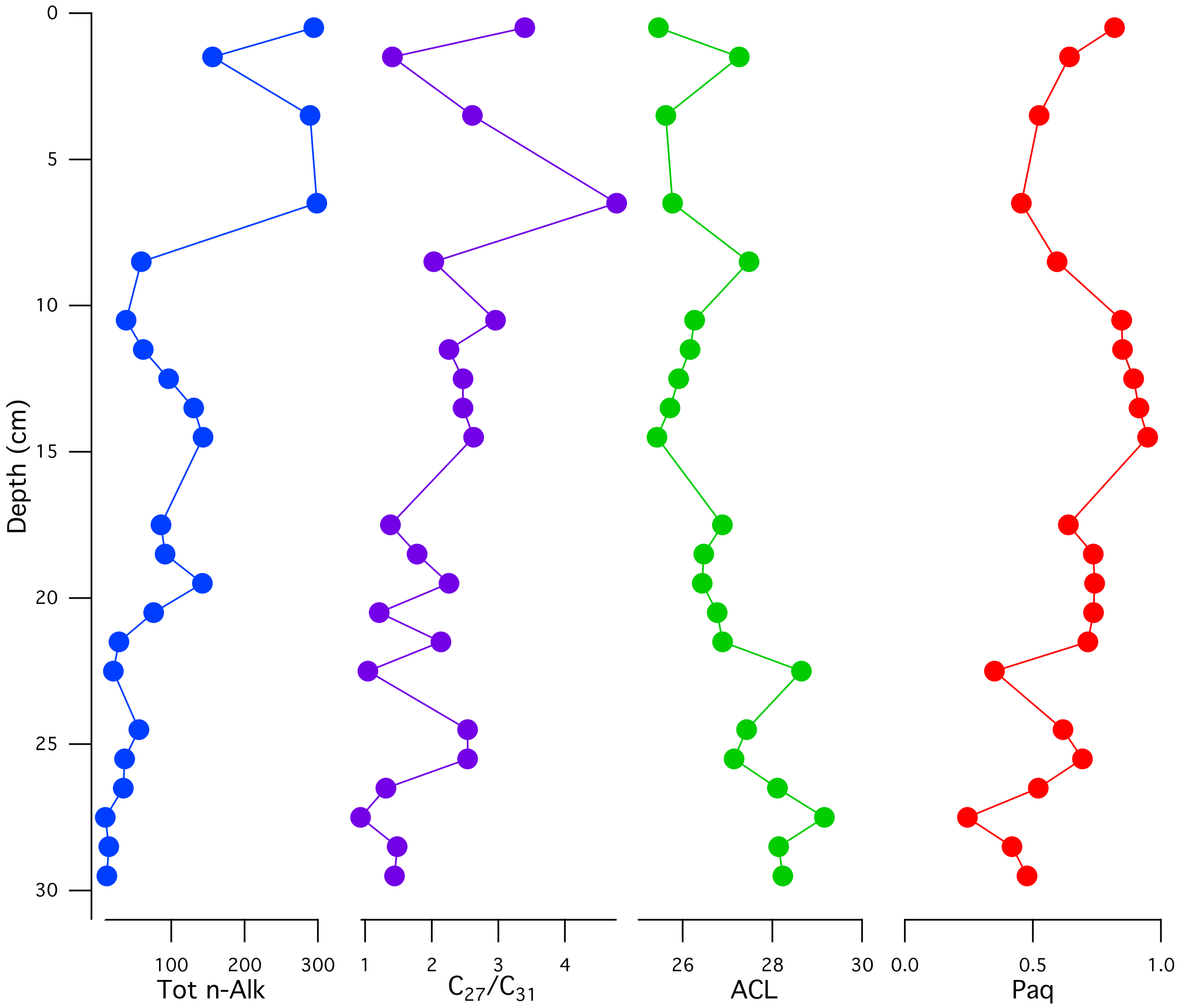


Figure 2. Total n-Alkanes concentration, Paq, C_{27}/C_{31} ratio and ACL in the sediment from Lake Trebecchi.

This preliminary results and data, covering the last 200 years, provide valuable information about the presence, the distribution and the sources of n-alkanes extracted from the sediments of Lake Trebecchi. This first information is essential to continue the study and the research with the aim of compare this data with other chemical and biological proxy.

5 NEXT Steps

In the next few months we are going to analyse other chemical proxies in the core. In particular we are going to try to retrieve direct information about changing in temperature in the last 200 years through the analyses of n-alkanes-specific hydrogen isotope ratio (δD) which has emerged as a powerful tool to track local to regional paleo-hydrological changes. The δD values of these organic biomarker molecules are directly related to δD values of meteoric water available to the biomarker source organisms. Moreover we are going to analyse GDGTs (Glycerol Dialkyl Glycerol Tetraether) and relate them with the MBT-CBT indexes. This method, through transfer functions, will help to reconstruct past continental air temperature based on subtle variations in the molecular structures of bacterial membrane lipids, the branched Glycerol Dialkyl Glycerol Tetraethers. This information will help us to have a deeper understanding of regional hydro-climatic changes and their impact on terrestrial and aquatic ecosystem.

6 Description of the dataset

The provided dataset is an excel file composed by 3 spreadsheets: “Q abs”, “Conc µg g^{-1}” and “Alk index”.
In the first one, where we have reported the absolute quantity of the measured n-alkanes, columns represent the depth (in centimetres) in which analyses have been done, rows represent the n-alkane analysed. In the second sheet the data of absolute quantity is transformed in concentration of n-alkanes expressed in µg g^{-1}.
In the last one we decided to calculate the following indexes: ACL, Paq, 27/31, (measured as shown in the report); then we reported in the first column the depth (cm), in the second the age, in the third the ACL index, in the forth the Paq index, in the fifth the 27/31 index and in the sixth the total concentration of all the n-alkanes measured in each depth.
The dataset is completely available at :
http://hdl.handle.net/11097/817ecf38-d4fe-46a0-91e3-11c7bd06a03e
https://data.lter-europe.net/deims/dataset/15043e47-cf2e-420d-b846-5cbf27b331c2

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