12. Carbon fluxes and Critical Zone observations in the Italian mountains

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12.1 General Introduction

The carbon cycle plays a central role in Earth's climate and in biosphere functioning, as it controls the amount of carbon dioxide in the atmosphere and thus the greenhouse effect. Besides the deep, "geological" and slow carbon cycle, associated with plate tectonics, volcanism, and surface rock weathering (e.g., Broecker, 2018), living organisms generate a "fast" carbon cycle with fluxes greatly exceeding the geological ones. Once more, this is an example where the emergence of a biosphere has dramatically modified the planetary cycles and processes, enhancing the rate of energy and matter exchange between the different reservoirs.

In this framework, an especially interesting concept was developed at the dawn of this century: the planetary "Critical Zone", that is, that thin living layer between the (almost) undisturbed rock matrix below and the top of vegetation canopy (NRC 2001, Giardino and Houser 2015). In this layer, which we can also call the "Earth living skin", one can witness the action of physical, chemical, geological, biological and hydrological processes that interact with each other at multiple space and time scales and support the terrestrial ecosystem.

Mountain regions participate in the global carbon cycle with their own and unique characteristics, and host especially interesting Critical Zones that are exposed to extreme weather conditions, frost-defrost cycles, and lately to the effects of widespread de-glaciation: reduction of seasonal snow cover, permafrost thawing, and glacier melting. In this sense, high-elevation Alpine areas are somewhat similar to Arctic tundra regions, also dramatically affected by temperature rise. At lower elevations, on the other hand, land-use changes, abandonment of traditional practices and unsustainable development are affecting the dynamics of vegetation and soils, with complex effects on the Critical Zone.

In the NextData project, we have supported and extended a network of ground measurement stations in the Italian mountains, devoted to the estimate of the carbon fluxes and to the study of the mountain Critical Zone. In this chapter we report on some of the measurement methods employed and on the measurement facilities that were installed, and discuss some of the results of the measurement campaigns.

12.2 Carbon fluxes in Alpine grasslands

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12.2.1 State of the art

Since centuries, a considerable part of the alpine region has been covered by semi-natural grasslands shaped by human agro-pastoral activities (Cruise, 1991; Ozenda and Borel, 2003). Currently, mountain agriculture faces a gradual abandonment with ongoing conversion of croplands and pastures to secondary forests (Alberti et al., 2011; Campagnaro et al., 2017). In the meanwhile, the European Habitats Directive (92/43/EEC) recognizes the alpine semi-natural grasslands among the priority type habitats thanks to considerable species richness and large number of rare species (Natural 2000, technical report 2008 12/24). The survival of this habitat, considered threatened, depends on the maintenance of the proper management practices (JNCC et al., 2007). Another important ecosystem service of the alpine grasslands is carbon (C) sequestration. In comparison to other grassland sites, high-altitude alpine grassland was characterized by one of the strongest C sink activity (Soussanna et al., 2004; Gilmanov et al., 2007). This service depends not solely on the site characteristics and proper management but is also highly sensitive to climate and its variation. Climate change in the Alpine chain follows different trends in respect to northern-hemisphere averages (IPCC, 2013). In particular, the increase in mean annual temperatures occurs at a double rate, amounting over the past century to 2 °C with major intensification starting from 1980s (Auer et al., 2007). Changes in the hydrological cycle have been documented, including trends to intensification of winter and spring precipitations in some areas (Schmidli and Frei, 2005) and, on the contrary, significant and progressive drying on the yearly basis in the others (Brunetti et al., 2006; 2009). It is projected that in XXI century the warming trend will continue depending on the emission scenarios. Under A1B scenario, 0.25 °C rising to 0.36 °C warming per decade could be expected accompanied by a decrease in summer precipitations and an intensification of the winter ones (Gobiet et al., 2014). How this climate changes will affect functioning and particularly C sequestration capacity of alpine grasslands is uncertain.

Recognizing the importance of the alpine grassland ecosystems and their fundamental role in the conservation of the biodiversity and in contributing to climate change mitigation, under the framework of the NextData project, there was re-activated one inactive eddy covariance site located in Eastern Alps - Malga Arpaco (Passo Brocon, Cinte Tesino, Italy). A second site, Torgnon, located in the Western Alps, was considered together with Malga Arpaco, to represent a small NextData network of alpine grassland eddy covariance sites with multiyear records. In this study we aimed at analyzing the main drivers of the inter-annual variation in net ecosystem exchange (NEE) in these two alpine grasslands located at the edges of the alpine chain and to characterize their resilience to changing climate. An ancillary aim was to derive the annual heterotrophic respiration (Rh) at both sites using radiocarbon measurements, which together with net primary production (NPP) could be used as an alternative tool to assess the annual C balance of the ecosystem.

12.2.2 Site characteristics

Malga Arpaco (IT-Mal, Fluxnet database) is a grazed grassland site located at 1730 m near Passo Brocon (46°11′402″ N; 11°70′334″ E); the area belongs to the Cinte Tesino municipality of the Trento Province. The territory is positioned in the Eastern part of the Alps in the southern part of the Dolomites. The mean air temperature is 5 °C with the annual rainfall ranging from 1100 to 1500

mm, falling primary in spring and autumn. In the winter months, from January to April, the site is generally under the snow cover. The territories surrounding the EC tower are rent by the local farmers and used as pastures from the mid-June to the end of August. Along the edge, the pasture borders with the *Picea* and *Larix* forests, which advance and colonize the patches of the abandoned grasslands located at the same height along Passo Brocon. The vegetation is dominated by good quality fodder *Poaceae* (*Festuca spp, Poa spp, Phleum spp*), consumed by grazers in summer and giving space to less palatable *Deschampsia spp*. The soil is classified as a sandy-loam alfisol (Soil Survey Staff, 2014).

The eddy covariance measurements (EC) have been started in Malga Arpaco in 2002 within the framework of the Greengrass project. The site was included in several European and Italian projects during the period 2003-2007. After that period the site was not used for EC measurements and it was re-activated and completely renewed in the framework of the NextData project starting from 2014 with regular EC measurements since 2015. EC set-up for Malga Arpaco consists of USA-1 three-dimensional sonic anemometer (Metek, Germany) for measurement of wind speed in the three components (u, v, w) and the sonic temperature, and LI-7500 open-path infrared gas analyzer (LI-COR, USA) for measurements of CO₂ and H₂O air densities installed at 3 m height. Additional sensors measure key meteorological parameters.

Torgnon (IT-Tor, ICOS, LTER, Galvagno et al., 2015) is a subalpine unmanaged grassland located in the north-western Italian Alps in the Aosta Valley region, at an elevation of 2160 m a.s.l. ($45^{\circ}50'40''$ N, $7^{\circ}34'41''$ E). The site, used as a pasture for livestock grazing in the past years, was abandoned in late 1990s, and only scarcely grazed until 2007. Dominant vegetation mainly consists of: *Nardus stricta L., Festuca nigrescens All., Arnica montana L., Carex sempervirens Vill., Geum montanum L., Anthoxanthum alpinum L., Potentilla aurea L. and Trifolium alpinum L.* During the growing season, the peak value of leaf area index (LAI) is on average 2.2 m² m⁻² and maximum canopy height is 20 cm. The site is characterized by a mean annual temperature of 3.1 °C and mean annual precipitation of about 880 mm. On average, the site is covered by snow (up to 90–120 cm) from the end of October to late May. EC measurements of CO₂ and H₂O fluxes, meteorological data collection, and temporary experimental analysis are carried out since June 2008 (Galvagno et al., 2013).

EC set-up for Torgnon site consists of: a CSAT3 three-dimensional sonic anemometer (Campbell Scientific, Inc.) for measurement of wind speed in the three components (u, v, w) and the sonic temperature, and a LI-7500 open-path infrared gas analyzer (LI-COR, Inc.) for measurements of CO_2 and H_2O air densities. Instruments are located at a height of 1.65 m above the ground and measurements are recorded at 10 Hz. Additional sensors measure several meteorological parameters. All the details on the instrumental system are found in Galvagno et al., 2013, 2015.

12.2.3 EC data processing and partitioning

Eddy fluxes are continuously calculated by computing the mean covariance between vertical wind speed and CO₂/H₂O densities, following the standard procedures as reported by the Euroflux methodology for both raw data processing and quality check (Aubinet et al., 2000; Mauder and Foken, 2004). Continuous time-series of NEE, GPP and Reco are obtained according to Reichstein et al. (2005). Furthermore, independent and standard estimates of filtered and gap filled NEE are also

available for Torgnon and Malga Arpaco in the FLUXNET2015 Dataset. For Malga Arpaco site, the EC data obtained in the years 2015-2017 are currently under gap filling process so that the data presented in this work should be considered as preliminary.

To determine the annual Rh from soil based on radiocarbon measurements, we applied the methodology proposed by Chiti et al. (2016). Briefly, in each of the two grassland sites, 10 soil samples were collected at each of the following depths: 0-5; 5-15; 15-30 cm. The samples were measured for their C concentration (ThermoFinnigan Flash EA112 CHN, Okehampton, UK) and the SOC stock derived from each layer based considering the bulk density (core method; Blake, 1965) and the rock fragment content. Three samples per layer and per sites were also measured by AMS for their ¹⁴C concentration 3MV CIRCE (Centre for Isotopic Research on Cultural and Environmental heritage of the second University of Naples, Italy). The annual Rh flux was then derived by the ratio between the SOC stock and the turnover time derived from the ¹⁴C measurements. The obtained Rh values were validated by a comparison with annual NEE and NPP values, which are linked by the following equation: NEE= NPP-Rh.

12.2.4 Results and Discussion

Inter-annual variability

The inter-annual variability of C balance in mountain grasslands is considerable as could be observed from the 8-year time-series of CO₂ fluxes in Torgnon (Figure 1).



Figure 1. Yearly NEE in Torgnon from 2009 to 2017.

The observed variability can be related to the strong impact of the inter-annual variability in multiple meteorological drivers (air and soil temperature, snow, PPFD, precipitations) on the ecosystem functioning at high altitudes. Indeed, in alpine grassland ecosystems, the time available for C uptake is confined in the short growing season occurring whiting long snow periods. Spring temperatures

impact the NEE of Torgnon and Malga Arpaco during the vegetation on-set period, in May (Figure 2).



Figure 2. Average NEE measured in May in various years of EC observations in Torgnon (a) and Malga Arpaco (b) plotted versus variation in monthly May air temperature.

This relationship seems to be however not direct but rather executed through the duration of the snow cover on the ground: the less is the snow cover duration - the longer and the higher is the spring C uptake (Figure 3). For Malga Arpaco, where May is generally snow-free, the average monthly NEE was still related to the height of the snow cover in March and April. Hence, the amount of snow in winter and spring could be used to simulate the spring carbon uptake timing and dynamics.



Figure 3. Average NEE measured in May in various years of EC observations in Torgnon (a) and Malga Arpaco (b) plotted versus variation in average snow cover in May for Torgnon and in March for Malga Arpaco.

In summer, air temperatures are not executing any visible influence on inter-annual variability of NEE in either site. Water availability, expressed in monthly precipitation rates, tend to increase the ecosystem respiration component in Torgnon in mid-summer (Figure 4). For Malga Arpaco, the relationship with precipitations is reverse: the more it rains - the more the ecosystem become productive in mid-summer. The origin of this divergence could be seen in different management of two sites. While in Torgnon, excluded from grazing, the abundant litter component accelerates in decomposition with rains, the grazed vegetation of Malga Arpaco in such conditions is instead favored to re-growth.

Hence, both ecosystems demonstrated to be very dynamic, responding quickly to changes in the local climate. Nevertheless, partitioning data from Torgnon site did not show progressive changes

. (a) -3.0 ς Υ -4.0 av. NEE, µmol m⁻²s⁻¹ -4.5 (b) -1.5 -2.5 -3.5 -4.5 Monthly precipitation, mm

in main components of the C balance – gross primary production and ecosystem respiration (data not shown) – highlighting the ability of the ecosystems to recovery from disadvantageous conditions.

Figure 4. Average NEE measured in July in various years of EC observations in Torgnon (a) and Malga Arpaco (b) plotted versus variation in July monthly precipitations.

12.2.5 Alternative partitioning methods

Rh flux derived from the ¹⁴C methodology for Malga Arpaco resulted in a value 0.7±0.2 Mg C ha⁻¹. Taking into consideration a mean value for the NEE of about 3.5 Mg C ha⁻¹ for this site (Soussana et al., 2007), and NPP of about 3.9 Mg C ha⁻¹ (this study), the obtained value is plausible and confirms the strength of the methodology for deriving annual heterotrophic efflux from soil based on a single soil sampling campaign. Similarly to what observed for Malga Arpaco, the annual Rh flux at Torgnon, derived applying the ¹⁴C methodology, resulted in a value of 0.8±0.2 Mg C ha⁻¹. While NPP is not

available for this site, the mean value for the NEE of about ~1.2 Mg C ha⁻¹ and above consideration on the importance of heterotrophic component for this site, suggest the derived Rh could be in a good agreement with other measurements. The method is promising because it does not dependent on continuous observations of fluxes, and could be applied for estimation of the approximate annual ecosystem C balance and partitioning in those locations where EC measurements are not available.

12.3 Effects of grazing and its cessation on aboveground and belowground functioning of alpine grasslands

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12.3.1 State of the art

Alpine grasslands are the products of thousands of years of interaction between human activity and specific environmental conditions: together with a continuous and intensive grazing of the herbivorous, mountain environment inhibits the development of arboreal vegetation while promoting herbaceous plants growth and short biological life cycles (Cruise, 1991; Ozenda and Borel, 2003). This semi-natural environment is characterized by a high biodiversity and hosts a large number of rare and endangered species (Wallis De Vries et al., 2002; Natural 2000, technical report 2008 12/24). In terms of C budget, it was demonstrated that managed grasslands may act as a sink for C, with mountain grasslands, being characterized by higher rates of C sequestration even during the extreme years like 2003 (Soussana et al., 2007). Because the main storage pools in grasslands are located belowground, the residence time of C in these ecosystems is potentially very high (Burke et al., 1997; Parton et al., 1993). At present time, mountain grasslands vulnerable environment is in a changing state, caused by the abandonment of the traditional pastoral activities and climate change, which is particularly pronounced at high altitudes (Alberti et al., 2011; Campagnaro et al., 2017). The decline in pasture lands and expansion of the forests have started prior to the first world war and is currently ongoing guided by a shift of agriculture practices to lowlands which are more profitable and easier for mechanization. Conversion of managed grasslands to other land use types (secondary forests or crops) is often associated with the loss of C from soil (Guo and Gifford, 2002; Alberti et al., 2011). The reason for that is uncertain but it is probably related to the interruption of complex interactions of soil organic matter mineralization and N cycle with defoliation by animals and excretal returns (Bardgett and Putten, 2014). Within NextData project we aimed at studying the biochemical and biodiversity transformations in soil and vegetation with the cessation of cattle

grazing. The study was conducted in Brocon mountain grassland site, where farmers apply different rates of grazing pressure on isolated patches of a mountain grassland.

12.3.2 Site characteristics

The study site, Brocon, is a mountain alpine grassland located 1700 m above the sea level in the eastern Alps (Cinte Tesino, Italy). The local farmers apply different management regimes for different patches under grazing: although the duration of grazing is changing from year to year, one portion of pasture is grazed for longer - on average 2 months (long grazing, LG) and another one – on average for one month (short grazing, SG). The grazed patches inside the fences are surrounded by the area excluded from grazing since 2002 (not grazed, NG). The site is equipped with an eddy covariance tower for continuous measurements of CO_2 and H_2O fluxes (Malga Arpaco site in Fluxnet database and Brocon site in NextData database).

12.3.3 Methods

At the end of July 2017, there were established 1 m² plots within the patches characterized by different management: 5 plots per patch were established in LG and SG patches and 4 plots – in NG. All plant species present within the plots were sampled for aboveground biomass estimation and botanical characterization. A portion of belowground organs of each species was sampled for biochemical analyses. The soil was collected in four angles of each plot to a depth of 15 cm. In the middle of each plot was taken a sample for belowground biomass estimation (Figure 5).



Figure 5. Map of the Brocon site, approximate borders of patches characterized by different grazing pressure are highlighted with different colors: Blue – Short Grazing (SG); Orange – Long Grazing (LG), patches are separated and surrounded by a non-grazed area (NG).

Once in the laboratory, plants were dried in the oven at 60°C and weighted. Green biomass and belowground organs were further milled to a fine powder for C and N isotope and elemental analysis on IRMS (Isoprime, UK) coupled to EA (CarloErba, Italy).

Soil samples were air dried, cleaned from roots and litter and sieved to 2 mm. Prior to biochemical analyses soils moisture was brought to 60% of their water holding capacity (WHC) and incubated for 7 days.

An aliquot was used for soil basal respiration determination following Badalucco et al., 1992. The incubation lasted 30 days, the mean values of the hourly CO₂ evolved after the 10 days of incubation were used as the basal respiration. Enzyme activity was measured according to Marx et al., 2001 and Vepsäläinen et al., 2001 with based on the use of fluorogenic methylumbelliferyl (MUF) and (AMC) substrates. The soil was analyzed for enzymes involved in the cycle of C (β -cellobiohydrolase, α -glucosidase, β -glucosidase, β -xylosidase), N (leucine-aminopeptidase and N-acetyl- β -glucosaminidase), P (acid phosphatase) and S (arylsulphatase). Lastly, butyrate esterase was determined as a proxy of endocellular activity. Microbial biomass C (MBC) and N (MBN) was determined by fumigation extraction (FE) method according to Vance et al., 1987. Ecophysiological indexes such as microbial (*q*mic, the ratio of microbial carbon to total organic carbon, TOC) and metabolic (*q*CO₂, the ratio of basal respiration CO_{2basal} to microbial biomass, MBC) quotients were calculated.

12.3.4 Results and Discussion

Fifteen years of grazing cessation induced some important changes in basic soil characteristics and in plant composition (Table 1). Particularly, cessation of grazing decreased the amount of organic C and total N in the soil. MBC and MBN followed similar trends observed for soil C and N.

Parameter	NG	SG	LG
Plant species found, all	14	15	22
Graminoids:Non-graminoids	06:08	05:10	05:16
Plant species found, average	6.7ª	7.6ª	10.8 ^b
Families found, average	5.5ª	5.8ª	7.6 ^b
Soil C, %	7.38ª	9.26 ^b	8.87 ^{ab}
δ ¹³ C soil, ‰	-26.17ª	-26.71 ^b	-26.46 ^b
Soil N, %	1.06ª	1.37 ^b	1.29 ^{ab}
δ ¹⁵ N, ‰	4.82ª	3.95 ^b	4.18 ^{ab}
MBC, ppm	2549.9ª	3729.4 ^b	3855.6 ^b
MBN, ppm	481.3ª	627.3 ^b	755.1 ^c
CO _{2basal}	0.95ª	2.62 ^b	1.81 ^{ab}

Table 1. Plant diversity and soil biochemical characteristics in plots subjected to different grazing regimes: NG – not grazed, SG – short grazing and LG-long grazing. MBC and MBN: microbial biomass C and N, respectively. The significance of difference between the treatments is indicated by letters at p<0.05.



Figure 6. N and C/N ratio of aboveground biomass in different species in grazed plots (LG and SG) plotted versus N and C/N ratio in non-grazed plots (NG).

Consequently, a common feature for almost all plant species was a higher content of N in aboveground biomass in plots subjected to grazing and a lower C/N ratio (Figure 6). Plants under SG regime tended to have more N and lower C/N in respect to those grown under LG grazing. Some non-graminoid species, like *Achillea millefolium* and *Alchemilla vulgaris* were characterized by a significantly higher δ^{13} C of plant material under grazing, suggesting a higher intrinsic photosynthetic water-use efficiency (i.e. the ratio between photosynthetic capacity and stomatal conductance) in confront to non-grazed analogous (data not shown). Together with a selective preference of good forages by grazers, it can explain a higher proportion of non-graminoid species in grazed plots, whereas with grazing cessation these species are suppressed by graminoids (Table 1).

% change in NG in respect to SG and LG					
Enzyme	Cycle	SG	LG		
6-cellobiohydrolase	С	-38.9*	-43.85*		
α -glucosidase	С	-7.0	-21.75		
β-glucosidase	С	-31.4*	-43.8**		
β-xylosidase	С	-32**	-34.4**		
butyrate esterase		+5.6	+2.5		
chitinase	N	-24.4	-29.5		
leucine-aminopeptidase	N	-21.7	-34.2*		
acid phosphatase	Р	-15.3	-19.8		
arylsulphatase	S	-5.7	-10.4		

Table 2. Percentage effect of grazing cessation on soil enzymatic activity in respect to SG and LG regimes. Significant differences at p<0.05 are marked with * and at p<0.01 – with **

Cessation of grazing negatively affected the activities of almost all soil enzymes with significant effects for enzymes involved in C and N cycles (Table 2). Mowing of the grassland in Apennines was associated with the decline in C-related enzyme activities due to the release of easily available carbohydrates through rhizodeposition in response to the biomass cut (Gavrichkova et al., 2010). Data of this experiment suggest that, although plants are also defoliated by grazing, its effect on Crelated enzymes is opposed to mowing. The patchily impact of grazing on plant biomass is probably not sufficient to stimulate the rhizodeposition, whilst the parallel release of N with excretal returns calls for C skeletons for its uptake and fixation. This leads to the release of enzymes involved in the degradation of complex C compounds and mobilization of N and C cycle under grazing (Table 2). Given that, soils under grazing were characterized by higher TOC values (Table 1) and higher MBCto-TOC ratio (microbial quotient, qmic), the last indicating a further positive trend in organic matter status under grazing. This apparent discrepancy could be explained by an exclusion of the protected or old soil organic matter from nutrient cycling in grazed grasslands and orientation of microbial activity towards "fresh" and already partially digested C provided by animals. In this view, the absence of N-rich excretal returns in non-grazed plots should lower the need for additional C and shift the microbial community to the degradation of the older soil C with its consequent losses from the system (Table 1). Furthermore, the comparison of two grazing regimes demonstrated that prolongation of grazing from one to two months is beneficial for both, microbial and plant communities. Microbial community becomes larger and more efficient in the use of C resources as demonstrated by higher MBC and lower CO_{2basal}-to-MBC ratio (metabolic quotient, qCO₂). The plant community instead grows in species richness and intrinsic photosynthetic water-use efficiency as demonstrated by botanical survey and stable C isotope composition of some species. The questions opened in this study on the influence of different grazing regimes on the mineralization of soil organic matter of different age and grade of protection should be studied on hoc.

12.4 Critical Zone in Alpine grasslands: the Nivolet Critical Zone and Ecosystem observatory (CZ@Nivolet)

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12.4.1 State of the art

The Critical Zone (CZ, NRC 2001; Elements, 2007; Giardino and Houser, 2015) is a heterogeneous environment at the Earth surface where chemical, physical, geological and biological processes interact with each other involving all environmental matrices such as rock, soils, water, air and living organisms. The CZ, also called the "living skin of the planet", is the transition zone between atmosphere, vegetation and the underground realm extending through the pedosphere into the unsaturated and saturate zone, and finally to the "undisturbed" bedrock. In the CZ water, carbon and energy cycles are tightly coupled with each other and determine exchanges of matter and energy throughout the terrestrial biosphere, providing essential ecosystem services such as water regulation and carbon sequestration. The study of CZ is a multidisciplinary research arena where different scientific communities analyze a multiplicity of aspects (e.g. geochemistry, geology, hydrology, ecology) to unravel the workings of the support system of all terrestrial life. Such studies are based on field measurements, taken in a network of CZ Observatories in the world (www.czen.org), remote sensing, and numerical modelling. In a sense, the Critical Zone is a prime example of the complex processes linking the geosphere, the biosphere and the climate (Rietkerk et al. 2011; White and Provenzale, 2018, www.to.isac.crr.it/gpss).

Global changes, including climate and land-use change, soil erosion and water/air pollution, affect the CZ in many complex and potentially disrupting ways. Soil loss and degradation, modifications of water and carbon cycles, biodiversity loss and ecosystem disturbances are impacting the CZ, potentially leading to a strong reduction in its ecosystem services provision. In high-altitude mountain areas and in polar regions, the CZ is a thin but essential layer between ice, permafrost, rock and the atmosphere, and it is especially exposed to the dangers associated with environmental and climatic changes.

12.4.2 Critical Zone Observatory at the Nivolet Plain, Gran Paradiso National Park

In Italy, no Critical Zone observatory existed prior to the effort described below. To quantitatively study the dynamics of the high-altitude mountain Critical Zone, in the framework of the NextData project, we have established new CZ observatories at the Gran Paradiso National Park (Provenzale, 2017), in three specific areas: the high-elevation (2600 meters a.m.s.l.) area of the Nivolet Plain, the recently deglaciated Valley of Nel (2200 meters a.m.s.l.), and the lower-altitude, grazed Valley of Noaschetta. In this contribution we focus on the Nivolet area, where we set up the CZ observatory

CZ@Nivolet. Figure 7 shows a picture of the Nivolet plain with its typical meandering stream. This area, covered with snow from November to June, is characterized by a complex environment of alpine pastures, oligotrophic lakes, peat bogs, rock outcrops and meandering streams, and it is the habitat of ibex, chamois, eagles and marmots. Domestic ungulates (cattle, sheep, goats) are brought up during the short mountain summer. The geological substrate includes areas with gneiss, carbonates, glacial deposits and alluvial soil. Two nearby weather stations provide daily records of temperature, precipitation and snow cover since more than 50 years.



Figure 7. The Nivolet Plain at the Gran Paradiso National Park, where the Critical Zone observatory CZ@Nivolet was established in the course of the NextData project. Water runs from right to left. Mean elevation is about 2600 meters a.m.s.l.

In this area, starting from 2016 we have conducted measurements on the carbon fluxes between soil, vegetation and atmosphere, using both a portable flux chamber method and a fixed eddy covariance station installed in 2017, shown in Figure 8.



Figure 8. The first eddy covariance station at the Nivolet Plain, Gran Paradiso National Park.

The "flux-chamber method", also generally called "enclosure-based method", is a widely used technique for measuring gas fluxes between soil and atmosphere. This method is based on measuring the temporally-varying concentration of the target gas (in this case, either CO₂, CH₄, H₂S, VOC and/or water) in a small chamber connected to an infrared spectrophotometer (IRGA) or a conductivity cell for H₂S.

The main features of this method are the relatively low cost, the portability, the possibility to estimate spatial variability and to perform direct NEE measurements (at daylight), or respiration measurements (using a dark chamber) of both soil (heterotrophic respiration) and vegetation (autotrophic respiration) during the day.

A few different configurations of the measuring device, and of the chamber in particular, have been developed for measuring soil-atmosphere gas exchanges with the flux chamber method (Parkinson, 1981; Norman, 1997; Pumpanen, 2004).

The static technique has been originally conceived for measuring soil respiration; the quantity of the emitted CO₂ was absorbed by a solution / sorbent placed inside the chamber. In this case, the sorbent (usually lime) is analysed at the time the vessel is placed on the ground and after a certain period of time. Currently, determination of emitted CO₂ by lime absorption has been mostly replaced by the on-site analysis by an infrared gas analyser, as such detection instruments have become portable, reliable and commercially available (Janssens and Ceulemans, 1998). The absorption technique is sometimes still used today because it presents several advantages: it is not expensive and it is very accurate as it produces only a small disturbance to the flux. On the other hand, it requires a long time for sampling and chemical analysis. The advantage of the adsorption method over the accumulation method is that it can integrate over periods up to 24 hours and can easily be applied simultaneously at tens or hundreds of soil chambers (Haber, 1958) at low costs.

Modern closed dynamic systems recycle the air from the chamber to the analyser and back, and can continuously monitor the increase in concentration. Portability and short measuring times in closed dynamic chambers allow the measurement of a high number of plots within a large area in a short time, and therefore the estimation of the heterogeneity of NEE or respiration over the area. Most of the commercial systems are now based on the closed dynamic chamber technique (LiCor, PPsystems, ADC).

In the closed-dynamic chamber configuration, the chamber isolates a portion of air above the measurer plot, sealing the soil (usually using a collar) so that only the flux exchanges between soil/vegetation and the air inside the chamber can occur and air cannot flow from inside to outside the chamber and vice-versa. A small sample of air is pumped constantly to the IR gas analyzer and then recycled inside the chamber. In the case of respiration measurements, if the target gas is emitted from the soil/vegetation, the concentration inside the chamber increases with time until saturation is reached and then the diffusion gradient becomes zero. The analysis of the concentration curve (calculation of the derivative of the curve for small time) allows to calculate the flux of the gas, which is obtained by solving the differential equation

$$\frac{dCO_2(t)}{(CO_2(t) - CO_{2soil})} = -\frac{\varphi}{Hc}dt$$

Where *Hc* is the height of the chamber, $CO_2(t)$ is the concentration of CO_2 inside the chamber at time *t* and $CO_2(soil)$ is the concentration of CO_2 in soil gas, considered constant. The solution of the differential equation leads to:

slope of the tangent line for t going to zero = $lpha~= arphi_{CO2}/Hc$,

as shown by Chiodini at al., 1998. In practice, the flux is derived as the slope of the regression curve taken for the first seconds of measurements, where the concentration curve can be approximated to a straight line, times the height of the chamber. A similar solution can be derived in case of NEE measurements when GPP prevails over respiration.

This method has been chosen in the field measurements at CZO@Nivolet as it is able to provide CO_2 measurements from soils regardless of the knowledge of the characteristics of the soils themselves and of the knowledge of the flow regime. In addition, this method does not require any empirical coefficient taking into account soil characteristics to transform the measured concentration gradient into a flux. Moreover, it is much faster than other enclosure-based methods, and the instrumentation is quite handy and easy to use. In practice, once the height of the accumulation chamber has been fixed, we can directly obtain the outflow of CO_2 from the ground, the latter being obtained from the slope (derivative) of the straight line (for low flow values) or of the initial part of the curve (for high flow values) of an increase in the concentration of CO_2 over time inside the chamber.

While measuring the gas fluxes, time of the day, GPS position, soil and air temperature, soil conductivity and radiance are simultaneously measured. All data are registered through a handheld Bluetooth device.

The operation of the instrument can be summarised as follows: the flux enters inside the chamber from the open part posed on the ground. At T_0 , concentration C = C air. If any gas is emitted from the soil by any mechanism (advection or diffusion), the concentration inside the chamber increases. A small pressure vent assures that the pressure inside the chamber equals the external pressure. A slow fan mixes the air with the aim of homogeneising the concentration inside the chamber, while a pump continuously aspires a little sample of air into the IR spectrophotometer.

The concentration inside the chamber is measured as a function of time. The following assumptions are used for obtaining flux estimates from the measurement system:

- Inside the accumulation chamber mixing is complete;
- The pressure inside the storage chamber does not change. This is ensured by the capillary tube at the top of the chamber;
- The gas, transported by a small pump, circulates between the storage chamber and the nondispersive IR instrument without altering the concentration inside the chamber.
- The system is isothermal.

Figure 9 illustrates the instrument, and Figure 10 shows one of the measurements performed during the NextData project.



Figure 9: scheme of the accumulation chamber and IRGA



Figure 10: Field measurements of gas fluxes at Nivolet Plain, Gran Paradiso National Park.

In addition to the flux measurements, in the CZ@Nivolet observatory we collected soil samples from different sites characterized by different geomorphology and geologic substrates: gneiss, carbonate and glacial deposits. Soil samples were collected from pits (see Figure 11) with profile description (horizons, color, structure, moist consistence, texture) performed on site (Soil Survey Staff, 1993). Soil samples were collected using a hand auger from the mineral soil surface to as deep as physically possible. As we were unable to manually auger to unweathered bedrock, the weathering profile extends deeper than sampled. The interface between the organic and mineral horizon was defined

as 0 cm. Samples were collected from the main horizons identified throughout the augerable profile and placed in a resealable plastic bag for storage.



Figure 11. Soil profile from the glacial deposit (left) and the gneiss site (right)

All samples were airdried and sieved to separate the fine component (< 2 mm) from the coarse fraction. A fraction (about ten grams) of this material was used to measure particle-size distribution by laser diffractometry using a Malvern Mastersizer 2000; a second fraction was used to measure pH (soil:water = 1:2.5) and conductivity (soil:water = 1:5); a third one was passed through a 100-mesh sieve (<150 μ m) and grounded with an agate mortar for chemistry; a fourth was kept as archive. The chemical analysis considered were: Total Inorganic Carbon (TIC) content, determined by volumetric measurements by a De Astis calcimeter, and Total Carbon (TC) and Total Nitrogen (TN) contents, measured by an Elemental Analyzer (Carlo Erba 1108). Total Organic carbon (TOC) was calculated subtracting TIC content from TC.

Most soils were developed in sandy or sandy loamy materials, with very small clay fraction (under 4% at the top of the profile) that was increasing with depth (up to 7%). The pH of topsoil for all the sites is lower than for deeper horizons; for the glacial and gneiss sites the conductivity decreases throughout the profile, whereas for the carbonate site it is higher at the bottom where the coarse fraction (> 2 mm) carbonate content is also larger. The TN content is very low (less than 0.1%) for all samples below 10-20 cm, while in the topsoil it is about 0.5%. In all sites, the topsoil was characterized by the highest TOC, which decreased regularly along the soil profile at the gneiss and glacial sites (Figure 12), indicating that a consumption and/or degradation of organic matter occurred mainly at the top of the profile. This trend is consistent with previous results (Chen et al., 2005; Scharpenseel et al., 1989; Jenkinson and Rayner, 1977). In particular, the transformation of soil organic matter during decomposition and the stabilization of organic carbon in the long-term soil carbon pool is one of the scientific questions related to CO₂ uptake, microbial respiration and carbon storage capacities in soils.



Figure 12. TOC concentrations (%) in bulk soil horizons along the soil profile.

12.4.3 Science questions

Besides the general issue of understanding the modifications of the Critical Zone induced by climate change and temperature rise, and the source/sink role of Alpine grasslands and Alpine tundra in the carbon budget, the first specific question that is being addressed by the CZ@Nivolet observatory is to identify whether different geological settings can influence the carbon fluxes. To this end, we identified four plots, each with side of about 50 meters, in the Nivolet area, characterized by different geological characteristics, namely: surface carbonates, gneiss, a mixed glacial deposit, and alluvial deposits close to the stream. In each plot, in summers 2017 and 2018 we performed a total of nine flux measurement campaigns, considering at least 24 replicas for each plot obtained in a time interval of about two hours. We used both a transparent chamber, to obtain the Net Ecosystem Exchange (NEE), and the same chamber shaded by a dark cover, to obtain the Ecosystem Respiration (ER), sum of plant/root and soil respiration. The Gross Primary Production (GPP), due to photosynthesis, was obtained by subtracting ER from NEE. For each replica, we also measured solar radiation, soil and atmospheric temperature, atmospheric pressure, and soil water content, to correlate flux variations with environmental variables. Vegetation surveys in each plot were performed, and soil samples were collected to determine soil chemistry and isotope characteristics in the laboratory.

A full account of the results will be provided in a forthcoming paper (Magnani et al. 2019, in preparation) and all data will be made available on the project portal. Here, we show in figure 13 the average NEE for two of the four plots monitored in the summers of 2017 and 2018, where the error bars represent the 1σ standard deviation. Notice the clear seasonal dependence of NEE, associated to both the intensity of solar radiation and the development and aging of vegetation. Analysis of the differences between the different plots and of the correlations with radiation, atmospheric and soil temperature and soil water content is ongoing and will be reported elsewhere.



Figure 13. Summer measurements of NEE in the "gneiss" plot (left, black points) and in the "carbonatic" plot (right, red points). Dates of measurements are indicated on the abscissae. Error bars are 12 standard deviations on the 24 individual measurements performed in each plot on each sampling date.

12.5 Conclusions

The carbon cycle is a crucial element of Earth System dynamics, as it links all different reservoirs (ocean, atmosphere, land and soil, vegetation, and mantle) and couples geospheric and biospheric processes, largely determining the Earth's climate.

In the mountains, ecosystems are often exposed to extreme climatic conditions and the biological activity is limited by the harsh environment. Here, understanding the sink/source role of the different ecosystem components, its temporal and spatial variability and the possible ongoing modifications generated by climate and land-use change is a primary research goal that has relevant practical implications, for example for assessing the health state of mountain grasslands and their role as a support system of ungulate populations. The NextData project has allowed to support existing monitoring stations, establish new ones (such as that at Gran Paradiso), and conduct new research that will continue in the coming years using the infrastructures installed so far. The data are made available on the specific portals, to allow the scientific community to benefit from the project outcomes. In particular, the NextData project allowed to establish a novel Critical Zone observatory in the Alps, the first one in Italy.

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