5.5. Organic Matter

Soil organic matter *(SOM) represents the remains of roots, plant material, and soil organisms in various stages of decomposition and synthesis, and is variable in composition. Though occurring in relatively small amounts in soils,* ***organic matter*** *(OM) has a major influence on soil aggregation, nutrient reserve and its availability, moisture retention, and biological activity.* ***Soil Organic Carbon (SOC) ranges from being the dominant constituent of peat or muck soils in colder regions of the world to being virtually absent in some desert soils.*** *Cultivated, temperate-region soils normally have often than 3 – 4 % SOM, while soils of semi-arid rainfed areas, such as in the WANA region, have normally less than 1.5 % SOM.*

Most laboratories in the region perform analysis for SOM, which can be measured by. either the loss after ignition method, i.e., weight change destruction of organic compounds by H_2O_2 treatment or by ***ignition*** *at high temperature, or by* ***wet combustion analysis*** *of soils by chromic acid digestion , which is the standard method for determining total C. Also, organic matter/organic carbon can be estimated by volumetric and colorimetric methods. However, the most common procedure involves reduction of potassium dichromate ($K_2Cr_2O_7$) by OC compounds and subsequent determination of the unreduced dichromate by oxidation-reduction titration with ferrous ammonium sulfate. This method is referred to as the* ***Walkley-Black method*** *(Walkley, 1947; FAO, 1974).*

While the actual measurement is of oxidizable organic carbon, the data are normally converted to percentage organic matter using a constant factor, assuming that ***OM contains 58% organic carbon****. However, as this proportion is not in fact constant, we prefer to report results as* ***oxidizable organic carbon, or multiplied by 1.33 as organic carbon.***

Apparatus

Magnetic stirrer and Teflon-coated magnetic stirring bar

Glassware and pipettes for dispensing and preparing reagents

Titration apparatus (burette)

Reagents

A. Potassium Dichromate Solution ($K_2Cr_2O_7$), 1*N*

- Dry $K_2Cr_2O_7$ in an oven at 105 °C for 2 hours. Cool in a desiccator (silica gel), and store in a tightly stoppered bottle.
- Dissolve 49.04 g $K_2Cr_2O_7$ in DI water, and bring to 1-L volume.

B. Sulfuric Acid (H_2SO_4) concentrated (98 %, sp. gr. 1.84)

C. Orthophosphoric Acid (H_3PO_4), concentrated

D. Ferrous Ammonium Sulfate Solution [$(NH_4)_2SO_4.FeSO_4.6H_2O$], 0.5 *M*

Dissolve 196 g *ferrous ammonium sulfate* in DI water, and transfer to a 1-L flask, add 5 mL *concentrated H_2SO_4*, mix well, and bring to volume.

E. Diphenylamine Indicator $(C_6H_5)_2NH$

Dissolve 1 g *diphenylamine* indicator in 100 mL *concentrated H_2SO_4*.

Procedure

1. Weigh 1 g air-dry soil (0.15 mm) into a 500-mL beaker.
2. Add 10 mL **1 *N* potassium dichromate** solution using a pipette, add 20 mL **concentrated H_2SO_4** using a dispenser, and swirl the beaker to mix the suspension.
3. Allow to stand for 30 minutes.
4. Add about 200 mL **DI water**, then add 10 mL **concentrated H_3PO_4** using a dispenser, and allow the mixture to cool.
5. Add 10 – 15 drops **diphenylamine** indicator, add a Teflon-coated magnetic stirring bar, and place the beaker on a magnetic stirrer.
6. Titrate with **0.5 *M* ferrous ammonium sulfate** solution, until the color changes from violet-blue to green.
7. Prepare two blanks, containing all reagents but no soil, and treat them in exactly the same way as the soil suspensions.

Calculations

$$M = \frac{10}{V_{blank}}$$

$$\textbf{Oxidizable Organic Carbon}\ (\%) = \frac{[V_{blank} - V_{sample}] \times 0.3 \times M}{Wt}$$

$$\textbf{Total Organic Carbon}\ (\%) = 1.334 \times \textbf{Oxidizable Organic Carbon}\ (\%)$$

$$\textbf{Organic Matter}\ (\%) = 1.724 \times \textbf{Total Organic Carbon}\ (\%)$$

Where:

M = Molarity of $(NH_4)_2SO_4.FeSO_4.6H_2O$ solution (about 0.5 *M*)

V_{blank} = Volume of $(NH_4)_2SO_4.FeSO_4.6H_2O$ solution required to titrate the blank (mL)

V_{sample} = Volume of $(NH_4)_2SO_4.FeSO_4.6H_2O$ solution required to titrate the sample (mL)

Wt = Weight of air-dry soil (g)

0.3 = $3 \times 10^{-3} \times 100$, where 3 is the equivalent weight of C.

Technical Remarks

1. **The conversion factor for organic carbon to total organic matter** for surface soils varies from 1.7 to 2.0. In the soils of arid and semi-arid regions; and a value of 1.724 (=1/0.58) is commonly used. The factors 1.334 and 1.724 used to calculate *TOC* and *OM* are approximate, and may vary with soil depth and between soils.
2. **For soils high in OM** (1 % oxidizable OM or more), more than 10 mL potassium dichromate is needed.
3. Soils containing large quantities of chloride (Cl), manganese (Mn) and ferrous (Fe) ions give higher results. The Cl interference can be eliminated by adding silver sulfate (Ag_2SO_4) to the oxidizing reagent. No known procedure is available to compensate for the other interferences.
4. The presence of $CaCO_3$ up to 50 % of sample weight causes no interferences.
5. **The Walkley-Black method for the determination of SOC** in soils gives about 89% recovery of carbon as compared to the dry combustion method. The conversion factor 0.336 was obtained by dividing 0.003, the milli-equivalent weight of carbon, by 89% and multiplying by 100 to convert to percentage. Chloride interference is eliminated by the addition of the silver sulfate to the digesting acid as indicated. The presence of nitrates and carbonates up to 5 % and 50 %, respectively, do not interfere.
6. **The concentration of H_2SO_4 should be about 6*M***. For this reason only 30 mL water are added. (10 mL $K_2Cr_2O_7$ solution plus 20 mL concentrated H_2SO_4 plus 30 mL H_20 give about 6 *M* H_2SO_4).
7. Air-dried soils seldom contain sufficient amounts of Fe (II) to cause interference. Water-logged soils often contain large quantities of Fe (II), but in most cases this can be oxidized by drying the soil samples prior to analysis.
8. Chloride is oxidized to chromyl chloride, which is volatilized, resulting in high OM values. If high amounts of Cl are present in the sample, add 15 g Ag_2SO_4 to 1-L H_2SO_4.
9. **Sulfuric acid readily absorbs water**. Therefore, use a fresh reagent.
10. **Elemental C** (e.g., charcoal) is not attacked by dichromate solution in this method.
11. Grinding of the samples is required only to reduce sub-sampling error. It is generally not necessary to pass the ground sample through a sieve (if required use a non-ferrous sieve).

Proper management, such as avoiding excess manure application and synchronizing application time with crop uptake, will ensure the most positive effects of manure addition on SOC storage and GHG emission (Johnson et al. 2005). Soil N_2O emissions are enhanced by spreading animal manure as a slurry, since 60–70% of N in slurry is present as NH_4^+, urea and uric acid, while solid manure and crop residues have larger content of less labile organic N materials. Moreover, slurry application of manure to soil surfaces can favour temporary anaerobic conditions leading to peaks in N_2O emissions (Vallejo et al. 2004; Mcswiney and Robertson 2005). In soils where the availability to microbial activity of labile organic material is limited, manure may produce more N_2O than mineral N fertilizers (Christensen 1983, 1985; Benkiser et al. 1987; Bowman 1990; Van Cleemput et al. 1992) and a combined application of manure and mineral fertilizers can lead to amplified N_2O emission rates.

9.2 Measurements of CO_2 and N_2O Fluxes from Soil

9.2.1 State of the Art on Soil Gases Measurements

Although agricultural soils are important source of anthropogenic CO_2 and N_2O, no alternative soil managements have been developed to limit their fluxes, particularly for N_2O. Since pedo-climatic conditions are key factors, a monitoring activity at territorial scale is needed, not only for testing different soil managements but also to obtain data from Mediterranean soil–crop systems. Freibauer (2003) has pointed out already that large uncertainties are present in the GHGs inventory for Mediterranean croplands due to lack of extensive monitoring activities.

Among alternative soil managements, minimum tillage, green and animal manure have been largely studied. Research on the use of compost in agricultural soils has been mostly focused on nutrition and environment aspects, i.e., OM quantity and quality, accessibility of organic contaminants and heavy metals, crops yield, soil microbial response. Fewer studies were devoted on GHGs emissions from soils following compost addition. Moreover, no examples are up-to-date present in literature for the use of catalysts in soils to structurally modify SOM and increase carbon fixation.

Monitoring GHGs fluxes from soil presents some difficulties. In the case of CO_2, it is difficult to discriminate among the different biogenic sources of CO_2 (see Sect. 9.1.2). The separation between SOM-derived and plant-derived CO_2 is essential to evaluate the real capacity of soil as source or sink of atmospheric CO_2. Also soil N_2O fluxes result from complex interaction among biological, physical and chemical factors, within a large spatial and temporal variability. Thus, the evaluation of soil fluxes of both gases is made difficult by methodological limitations (Kuzyakov 2006; Groffman et al. 2006), and high spatial and temporal variability in

field-scale, particularly for N_2O (Clemens et al. 1999; McSwiney and Robertson 2005; Wagner-Riddle and Thurtell 1998).

Models are increasingly used to quantify C and N gas fluxes at territorial scale, especially when agricultural policies are to be developed. However, there are few long-term data sets, particularly for N gas fluxes, to be used in model validation (see also Chap. 2). The current IPCC (2007a, b) methodology for producing national inventories of N_2O from agricultural land is based on the study of Bouwman (1994) and it assumes a default emission factor (EF) of 1.25% for soil-added nitrogen. This approach does not account for climate, management practices, irrigation, soils and crop types, and other variables. Moreover, the data considered by Bouwman (1994) were mainly referred to croplands under temperate climatic conditions. Thus, more experiments are required to obtain a correct evaluation of N_2O emissions from agricultural lands under different climatic regimes at regional and national scale.

Due to such shortcomings, new experimental designs for soil gases monitoring must be planned to obtain data with large time resolution. Spatial and temporal variabilities depend on the physical–chemical factors that affect all soil biological processes inducing the production of CO_2 and N_2O. Much of the challenge arises from the fact that small areas (hotspots) and brief periods (hot moments) often account for high fluxes. In the last decades several experiments were conducted to understand the factors controlling the CO_2 and N_2O fluxes from soils (oxygen content, nitrogen availability, soil moisture and texture, and so on). However, the complex regulation of these factors, including soil management practices, creates hotspots and hot moments that are difficult to quantify and model. Due to technical restrictions, most attention was focused in determining the hotspots, particularly for N_2O production and emissions. N_2O hotspots in soils involve the interaction among patches of organic matter and physical factors controlling oxygen diffusion in soil, and transport and residence time of N_2O in soil pores. Thus, a series of plant and soil factors, e.g., rooting patterns and soil structure at small (0.1–10 m) scales, topography, hydrologic flow paths and geology at larger (>1 km) scales, need to be considered to understand the spatial distribution of hotspots. Currently, soil N_2O emissions predicting models are calibrated on the basis of spatial variability. However, their reliability to predict temporal variations is seriously undermined due to the very few data available in literature to calibrate these models over time.

The hot moments concept has been known since long time but hardly investigated by continuous monitoring, particularly in the small time scale, since few experiments are based on high-time-resolution measurements systems [dynamic chambers, Tunable Diode Laser (TDL) associated with eddy covariance technique]. The large part of data produced up-to-now, are referred to manual chamber measurements limited in temporal resolution.

Despite the increasing popularity of the eddy covariance technique to assess ecosystem C exchange and, recently, also N exchange by means of TDL, classical static or dynamic chamber methods remain the most useful tools. This is due to some limitations of the eddy covariance technique for C exchange. Mainly, micrometeorological techniques are only able to obtain the total CO_2 fluxes and cannot partition total flux into its individual sources (Buchmann 2002). Conversely,

chamber methods allow CO_2 fluxes to be measured directly from soil. Moreover, the eddy covariance technique has large purchase and installation costs, particularly for TDL equipment, even though this has the additional advantage to provide soil exchange also for N_2O and CH_4 gases. Some studies have simultaneously used eddy covariance and chamber methods to separate net ecosystem CO_2 exchange from soil respiration (Lavigne et al. 1997; Dore et al. 2003), as well as to correct the fluxes obtained by eddy correlations during night periods (Anthoni et al. 1999; Law et al. 1999; Dore et al. 2003).

Factors affecting time variation of soil gas fluxes are different: management, root exudates, drying and rewetting, etc. Factors affecting time variation of soil gas fluxes are different: management, root exudates, drying and rewetting, etc. Contrary to current understanding that daily CO_2 dynamics are attributed to day–night variation of soil temperature, the process is also associated to fast decomposition processes that release easily decomposable substrates and enhance CO_2 production, thus resulting in diurnal CO_2 dynamics (Kuzyakov 2006). In agricultural ecosystems, pulse emissions of N_2O are also frequently associated with fertilizer additions, organic treatments and following re-wetting after periods of prolonged drought (Davidson et al. 1993; Ranucci et al. 2011).

9.2.2 Monitoring System in Field Plots

Within the MESCOSAGR project, soil CO_2 and N_2O fluxes were measured for each soil treatment in both the experimental sites of Torino (Tetto Frati) and Napoli (Torre Lama). Detailed information of study sites and experimental design are described elsewhere (Chaps. 3 and 4).

Two periods of gas-fluxes measurements (May 21–28 and July 16–24) were carried out in Torino (Tetto Frati) during the maize crop in 2008. The first period in May began immediately after nitrogen fertilization (where scheduled) and sowing; the second period was near the completion of maturity of maize plants. Gas emissions from the Napoli site were measured for all soil treatments during the autumn–winter period after the 2007 maize crop (October 2007–March 2008) and for the 2008 maize cropping season (May–August 2008). Conversely, the gas fluxes from soil plots treated with the water-soluble biomimetic catalyst (see Chaps. 3 and 4) and under wheat cropping were monitored in the period December 2007–August 2008.

Soil CO_2 and N_2O emissions were measured by means of an automated closed-chamber system coupled to a 1412-Photoacustic Field Gas Monitor. The analytical system provided high-time resolution of gas fluxes data, being able to perform day-long analytical cycle of 10 min for each chamber. Before the measurements cycle in the Torino site and frequently (each month) in the Napoli site, tests to evaluate fluxes variability in space were performed. Since it was always low (coefficient of variation less than 100%), one or two chambers were placed in soil for each treatment. Each chamber provided daily, on average, 10–12 measurements.