ESTIMATION OF NITROGEN AND CARBON LOSS DURING COMPOSTING PROCESS OF OLIVE TREE LOPS AND CONTRIBUTION TO GREENHOUSE EFFECT

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ABSTRACT: The basic objective of the study was to quantify nitrogen and carbon loss during composting in order to understand the process and reduce potential adverse environmental impacts. Nitrogen and carbon loss was determined by the difference between the amounts at the beginning and at the end of the composting. It was observed that all materials were characterized by a reduction of C from 35 to 65%. The reduction of N was much higher than C loss (N loss was between 62 to 73%). The highest losses for N and C were recorded for the buckets containing OTL only, while the bucket containing OTL and seaweeds the least. The reduction of C was due to its transformation in CO_2 and CH_4 and their release into the atmosphere. Nitrogen can be lost from the mass of materials in runoff and by nitrate leaching composting. Thus, from the experimental point of view it was demonstrated that composting is not a particularly environmentally friendly method of biomass exploitation, due to significant production of greenhouse gases (GHG), such as CO_2 and CH_4 . The study integrates the findings of different investigations from the literature with field measured data in order to obtain a more comprehensive framework representative of the residues under study.

Keywords: agricultural residues, biomass, carbon dioxide (CO₂), composting, environmental impact

1 INTRODUCTION

The difficulties associated with Waste Management (WM) can be diminished or even erased, if an added value can be attributed to them. Composting is one of the natural bioprocesses capable of treating organic wastes through microbial activity. Composting can destroy pathogens, converts nitrogen from unstable ammonia to stable inorganic forms, reduce the volume of waste, and satisfy the needs for fertilizer in agriculture [1, 2].

The most important factors affecting composting include temperature, moisture content, C/N ratio, degree of aeration, Ph level, and the physical structure of the waste material. Furthermore, compost maturity and stability are the key factors of the bioprocess. Several authors have concluded that using a single parameter as a maturity index is insufficient and that amalgamation of several parameters is usually needed. Various physical, biological and chemical parameters have been used to monitor the quality and maturity of the compost, including C/N ratio, NH₄/NH₃, CO₂ evolution, pH, electrical conductivity, cation exchange capacity, watersoluble carbon, Dewar flask self-heating capacity, oxygen uptake rate and the production of humic substances in the finished product, as well as, a germination index to measure the phytotoxicity as a reliable indirect quantification of compost maturity [3, 4, 5]. Monitoring of the composting conditions during the bioprocess and the changes in the physicochemical characteristics confirm that satisfactory composting occurs after approximately 12 weeks [6]. Thus, composting has been concerned with the efficient and economic production of a product, while functioning within a larger process-oriented approach to solid WM [7, 8].

Aerobic decomposition results in emission of CO_2 and H_2O . Green House Gas (GHG) emissions from the composting process are highly dependent on the feedstock, which ranges from green wastes to Municipal Solid Waste (MSW), to manure. Waste streams with a higher Degradable Organic Carbon (DOC) will result in higher GHG emissions, while wastes with a lower decay constant rate, will require a longer period of composting, which may cause a difference in the operational requirements to compost that waste stream.

Theoretical calculations by White [9] estimated approximately 0.323 ton CO_{2-e}/ton of mixed waste, while Lou [10] estimated a value of 0.284 ton CO2-e/ton of mixed waste, taking into account the emissions from operational activities. Practical GHG measurements from alternative studies have produced emissions from composting operations of 0.183 ton CO_{2-e}/ton of mixed waste [11, 12], which are lower than those predicted from theoretical calculations. This may suggest that theoretical estimates overvalue the importance of operational activities on the impact of composting on GHG emissions. Composting tends to occur via windows composting or aerobic in-vessel composting, the former tending to have lower associated operating emissions [9, 13]. Emissions from operational activities vary with reports due to the type of composting operations, the amount of waste treated and other variations. Thus, an average emission from operation of composting is difficult to quantify. As a brief indication of the emissions from window operations, White [9] reported 0.071 MJ/kg waste, Baky and Eriksson [14] estimated 0.00151 MJ/kg, and Franklin Associates [15] estimated 0.134 MJ/kg waste.

Recently, there has been renewed interest in the emission of N_2O from composting [16, 17]. N_2O can be produced by either incomplete ammonium oxidation or via incomplete denitrification [16]. Results of N_2O generation have been mixed. He [17] reported high emissions at the beginning of composting and negligible amount after the initial 2 days, while Beck-Fris [16] reported higher emissions with time. Little is known regarding N_2O emission, however the fact that it has a GWP 310 times that of CO_2 makes its study a necessity [18].

Despite potential CH_4 and N_2O emissions, these are usually not taken into account in C budgeting. In fact in the IPCC Guidelines for National Greenhouse Gas Inventories [18] and the Australian Methodology for the

Estimation of Greenhouse Gas Emissions and Sinks [19]. only CO₂ is assumed to be emitted during composting. Even so, although this CO_2 is climate active when released, it is generally not considered when it comes to GHG accounting. This is due to the general consensus that CO₂ from composting is of biogenic origin and hence does not add to the overall GHG emissions that contribute to global warming [18]. Therefore, when C accounting is performed by composting facilities, their GHG contribution is a result of operational activities, as opposed to the actual decomposition process. Nevertheless, there are some that advocate the inclusion of all GHG emissions derived from non-fossil C [20]. The rationale behind this inclusion is that the climate responds the same whether the source is fossil or nonfossil C and thus all emissions should be accounted for, on a like-for-like basis.

Thus, from an environmental perspective, the negligence of composting contribution to GHG emissions is questionable, especially from a Life Cycle Analysis (LCA) approach. This is particularly relevant to centralized composting systems where operational activities are energy consuming [21]. It should be noted that some centralized composting facilities are driven to produce high quality compost that can be used for land application [8, 22].

Nonetheless, it can be argued that the production of compost can help mitigation GHG [10, 18, 19] by:

- Decreasing the need of chemical fertilizers and pesticides; thereby reducing GHG emissions from the use of fossil fuel associated with their production and application.
- Allowing, for more rapid growth, thereby increasing C uptake and storage within the plant. Studies have shown the increase in biomass of plants growth with compost application. This is a form of C sequestration which removes CO_2 from the atmosphere.
- Sequesting C in soil that has received compost application. The USEPA [23] estimated that approximately 50 kg C (183 kg CO₂) sequestered per ton of wet compost. On a large scale, this may be significant.
- Improving tillage and workability of soil (thereby reducing emissions from fossil fuel that would otherwise be used to work the soil).

In this study, Olive Tree Lops (OLT) were cocomposted with two different types of organic materials (grass and seaweeds), into plastic experimental buckets. It should be noted that these materials have not been adequately examined in the field of composting, but they are major agricultural - natural residues and their study is particularly important for the environment.

The composting process was developed during two different periods (winter and summer). The first part of the process started during the winter and stable and mature composts were produced after approximately five months (February – June). Three buckets were filled during the winter period, as follows: C1 with OTL only; C2 with OTL and grass; C3 with OTL and seaweeds. The second part of the experiment was started during the summer period and a stable and mature compost was received three months later (June – August). A new bucket, C4 with OTL only, was filled during this period, in order to be compared with the corresponding one of the winter period.

It was observed that, for all mixtures the C content reduced from 45 to 65%. The highest C loss recorded for the buckets containing OTL (bucket 1 and 4), while the less marked the bucket containing OTL and seaweeds (bucket 3). N loss was much greater than C loss, since it was close to 62 to 73%. The most significant N loss was observed, at the buckets 1 and 4 (OTL), while the smallest losses were recorded for buckets 2 and 3 (grass and algae, respectively).

Furthermore, the study integrates the findings of different investigations from the literature with field measured data in order to obtain a more comprehensive framework representative of the residues under study. The results may help public administrators to better understand the suitability of using LCA tools when dealing with agricultural waste management strategies.

2 AGRICULTURAL RESIDUES IN THE EU

2.1 Assessment of availability

In Europe there are great difficulties to produce harmonized biomass assessments due to the lack of georeferenced databases of forests and agricultural field residues covering the whole continent and made with standardized procedures. Environmental sustainability must not be forgotten, especially in the case of forests for which environmental concerns becomes even more important. Different studies have revealed that the environmental effects of biomass harvesting and field biomass removal depend upon different factors such as the type of residues removal on organic soil matter and soil erosion has been investigated by Mann [24, 25] amongst others. These authors investigated the influence of different residue management practices on the soil fertility of fast growing forest plantation in Southern Europe. Evaluation of agricultural and forest biomass residues was made for a total of 11 EU countries comprising 77% of the total EU territory, and Norway [26]. The EU countries taken into consideration were: Germany, Poland, Spain, Portugal, Italy, France, Greece, Sweden, Finland, Denmark and Austria. The biomass resources considered had been produced in the agroforestry sector as a consequence of field operations. Agricultural and forest field by-products (residues) were produced in croplands and forests which have, up to the present date, little or no commercial demand.

Agricultural field by-products are divided in two categories: herbaceous and woody by-products. Herbaceous by-products are considered to be those crop residues, which remain in the field after the crop is harvested. Their nature is diverse, depending on the crop, method of harvesting, etc. Woody by-products are those produced as a consequence of pruning and regenerating orchards, vineyards and olives. Normally herbaceous crops are cultivated on arable land, whereas woody plantations are considered permanent crops. Forest byproducts usually consist of branches, tops, bushes, understory vegetation, and in general, wood not exploited for conventional uses such as timber sawing, pulp or board production. Consequently, the different processes applied to stands in distinct parts of the cycles, such as brush removals, first thinnings, intermediate thinnings and regeneration fellings, generate different forest byproducts.

2.2 Production of agricultural residues in the EU

Large differences in terms of cultivated area and types of crops and yields are observed between EU Member States (MS), due to the climate conditions, specific soil condition and farming practices. Large amounts of agricultural residues are generated from agricultural crop production and partially remain in the field after harvest. Residue production depends on a number of factors that include the types of crops, crop rotation, crop mix and agricultural practices.

The availability of residues depends on the amount that can be removed from land to maintain land fertility and on their competitive use for agricultural or industrial purposes. The total amount of crop residues produced in EU27 every year was estimated at 258 M dry tonnes/year on average, based on the residue yield and crop area [26]. Based on the sustainable removal rates of crop residues, residue-to-crop yield and seed and straw moisture content, the amount of collectable crop residues was estimated. The results show that 111 M tonnes dry matter of crop residues/year can be collected, on average, in EU27. However, this amount can vary between 86 to 133 M tonnes dry matter/year depending on crop residue production [27].

The residue biomass is commonly estimated by the use of Residue to Product Ratios (RPR). The residue to product ratio is a key issue in every evaluation and should be used carefully as it is typically applicable only at a regional or local level, and this has been stressed in some papers [28].

Frequently, in making agricultural by product estimates, a constant straw to grain ratio is assumed. This assumption may not always be accurate because strawgrain ratios can vary greatly across environments and genotypes. Some authors report straw to product ratios higher in Central and Northern European countries than in those in the South of the continent [28] and more generally, higher ratios in wet climates than in dry ones [29]. In general, RPR values available are scarce and it has been difficult to find for all the evaluated countries. The values utilized for Spain, France and Portugal were taken mostly from unpublished works. Values for Italy and Greece were obtained from Di Blasi [29] and Nikolau [28], respectively.

As can be deduced from **Table 1 and Table 2**, 364.50 Tg y⁻¹ of forest and agricultural residues are estimated as 'potential resources' in the 11 EU countries considered (77% of the EU 27 territory) and Norway. After the application of technical and environmental restrictions, the available resources are calculated to be 205.33 Tg y⁻¹ (56.33% of the estimated biomass potential).

Most forest biomass is located in Northern EU considered (63.07% of the potential and 62.95% of the available resources) whilst most of the agricultural residual biomass is in Southern EU countries (52.69% and 55.18% respectively, for potential and available resources). Globally, the biomass resources are very similar (30.83% of the total available biomass is in Southern EU countries) [26, 27, 28, 29].

Agricultural residues in Greece amount to several million tons per year, while OTL ranks first with 1.4 - 3.0 million tons per year. After the removal of the thicker woods, the rest are burned in the countryside by farmers causing, except from energy losses, severe air pollution problems (greenhouse gases, micro particles, etc.). It is

estimated that approximately 3.3 million tons CO_2 are released by burning. Arguably, a significant improvement on this existing practice can be brought about if OTL is used as compost feedstock.

 Table 1: Forest biomass resources estimated in the evaluated countries

Country	Potential (Tg vr ⁻¹)	Available (Tg vr ⁻¹)	MARV (Mg ha ⁻¹ v ⁻¹)
Sweden	20.68	10.43	0.49
Finland	13.59	6.94	0.23
Germany	9.54	4.27	0.26
Austria	5.26	2.63	1.08
Norway	8.6	4.33	0.46
Poland	4.11	2.05	0.29
Denmark	0.74	0.37	0.88
SUBTOTAL	62.52	31.02	-
France	13.43	7.75	0.63
Spain	10.55	4.77	0.44
Italy	7.49	4.01	0.53
Greece	2.90	1.09	0.53
Portugal	2.23	0.64	0.29
SUBTOTAL	36.60	18.26	-
TOTAL	99.12	49.28	-

 Table 2: Agricultural biomass resources estimated in the evaluated countries

Country	Potential (Tg yr ⁻¹)	Available (Tg yr ⁻¹)	MARV (Mg ha ⁻¹ y ⁻¹)
Sweden	5.93	3.11	4.19
Finland	3.08	1.12	1.9
Germany	67.34	42.56	6.85
Austria	1.85	0.83	0.26
Norway	6.25	3.79	5.00
Poland	28.09	10.36	2.87
Denmark	12.99	8.17	5.80
SUBTOTAL	125.53	69.94	-
France	78.39	49.81	4.24
Spain	26.22	12.84	1.23
Italy	25.44	16.94	2.35
Greece	7.42	4.82	2.09
Portugal	2.38	1.70	0.96
SUBTOTAL	139.85	86.11	_
TOTAL	265.38	156.05	-

3 COMPOSTING

3.1 Maturity and stability parameters

The recycling and utilization of organic wastes and by products through development of an economically viable, socially accepted and eco-friendly technology is urgently needed for the reason that the large scale accumulation of these wastes will increase pollution and also pose disposal problems. However, the substantial quantities of humus in these wastes may have great value for maintaining soil health. Composts prepared from different organic wastes differ in their quality and stability, which depend upon the composition of raw material used [30]. Compost quality is closely related to its stability and maturity, which cannot be established by single parameter [31]. Several parameters such as temperature, organic matter loss, C/N ratio, cation exchange capacity, humification index and seed germination index have been proposed for evaluating compost stability by different authors [32, 33, 34, 35, 36]. Despite all the proposed methods to establish the degree of maturity and stability of composts, no single method can be universally applied to all composts due to variation of materials and composting technology [35, 37]. The study by Raj and Antil [38] concluded that using a single parameter as a maturity index of composts made from farm and agro-industrial wastes is difficult.

Also, our findings suggest that compost maturity should be assessed by measuring two or more compost parameters, and that parameters of compost maturity need to satisfy the following threshold values: OM loss >42%, C:N ratio <15, Cw:Norg ratio <0.55, HA:FA ratio >1.9, HI >30%, CEC/TOC ratio >1.7 and GI >70%. As per the above maturity and stability parameters, composts enriched with agro-industrial wastes matured earlier as compared to compost prepared without any enrichment.

3.2 Composting of different starting materials

As has been mentioned above, compost is a valuable resource as a soil fertilizer, providing a high content of macro- and micronutrients for crop growth, and represents a low-cost alternative to mineral fertilization [39]. A practical use of composted materials in agriculture requires good knowledge of its maturity and the level of organic matter (OM) stabilization reached at the end of the composting process. The application of unstable OM on soil may produce competition for oxygen between microbial biomass and plant roots. This fact can deprive plant roots of oxygen and lead to the production of H₂S and NO₂. Another problem is the possible nitrogen starvation of plants as microorganisms scavenge soil N to make up for the deficit resulting from the application of unstable OM with high C/N ratio [33]. Moreover, the emission of ammonia and the presence of other phytotoxic substances like phenolic compounds, ethylene oxide and low-molecular weight organic acids that are synthesized during the decomposition of unstable compost in soil are responsible for compost phytotoxicity [40].

The application of chemical parameters to assess the stability of compost is a common practice in research on composting [41, 42, 43, 44]. Some of these parameters are not considered good indicators of compost stability because they poorly describe the evolution of OM quality during composting; this is mainly due to the utilization of strong oxidants or strong bases which break down carbon not readily available for microorganisms [45]. The use of Dissolved Organic Carbon (DOC) as a stability parameter proved to be closer to the real request of energy by the microbial community during composting [45]. DOC generally contains organic compounds with different susceptibilities to microbial degradation and different phytotoxic properties. For this reason, DOC composition may have an important role in determining the stabilization process. The NH_4^+/NO_3^- ratio has also been proposed to estimate the compost stability. At the end of the composting process, the content of NO_3 should be higher than that of NH₄⁺, indicating that the process has been performed under adequate aeration conditions. Nitrifiers are a low competitive community becoming effective when the temperature of the mass under composting decreases and the readily degradable substances (DOC and soluble N) are low [46]. More recently, besides the CO₂ evolution, many authors have studied the relationship between microbial activity and composting time by means of the OUR during OM degradation [47, 48, 49]. Tremier [50] used the respirometric technique to highlight the important role played by substrate biodegradability in compost evolution over time.

The adoption of different sludges in the mixtures strongly affected the OM mineralization course during the composting process. The addition of food processing waste strongly enhanced the OM mineralization and the Norg losses, compared to the addition of a digested sewage sludge. The parameters which are often adopted in the description of the compost stability like the C/N, the DOC content, and the NH₄⁺-N/NO₃⁻N ratio, did not well describe the relationship between composting time and stabilization level reached by the mass. The study showed that the kind of mixture and the time of composting strongly affected these parameters. This was particularly evident regarding the mineral nitrogen course: nitrate losses were important, and were probably due to the denitrification operated by fungi especially in the last part of the composting process. Mineral nitrogen appeared to be the rate limiting step in the composting process of more stabilized raw materials as digested sewage sludge. The regression analysis showed that the measurement of the OUR by means of a standardized test proved to be a valid tool to describe the stabilization level variation during the composting process. The adoption of this test in a non-limiting nutrient environment that stimulates microbial growth, gives the real extent of potential mineralizable OM following the addition to a nutrient rich environment as soils can be [51].

3.3 Engineering research

Most of the engineering research on composting treatments aims to identify how the waste characteristics and the composting conditions influence both the composts quality and the environmental impacts of composting. Recently, researchers started considering the active phase of composting according to its main ruling processes i.e. biological activity and heat and mass transfers. Taking into account the different natures of waste, this progress led to identify intrinsic properties, which characterize the waste regarding a specific behaviour. Then, the determination and the quantification of these properties allowed the improvement of mixture formulations and the adjustment of composting conditions.

The questions of biodegradability and stabilization illustrate the evolution described above. At first, most studies aimed to test the relevancy of numerous indicators in order to predict compost stability. Many papers dealt with the differentiation between maturity and stability, maturity being related to the presence or absence of phytotoxins whereas stability was related to microbial respiration activity of compost [52]. Thus, respirometric methods, based on the measurement of oxygen consumption or carbon dioxide production rate, developed. Then, in order to predict wastes behaviour in composting and adjust treatment conditions, researchers also interested to the biodegradability of the organic wastes. Taking into account the higher oxygen demand of wastes compared to the one of composts, static respirometric methods were shown to underestimate oxygen required for stabilisation [53]. Nowadays, most of the authors dealing with the biodegradability of organic waste use a dynamic respirometric method i.e. with a continuous aeration [54]. However, as underlined by

Berthe [55], the dynamic methods [56, 57, 58] still differ to each other regarding the control of temperature, moisture and oxygen supply. Thus, Tremier [59] and Berthe [55] control the temperature, the moisture and the oxygen supply at the same time. In contrast, Scaglia [57] and Adani [56] simulate a composting treatment in which the temperature increase results from the material selfheating. Although temperature profile in composting simulation seems more realistic than in a thermostated bath, composting simulation does not optimise air distribution leading to a non-homogeneous aeration of the composting material. These methods also differ regarding the indicator used to characterize the biodegradability. Berthe [55], de Guardia [60] and Tremier [58] used the cumulated amount of oxygen consumed during biodegradation, whereas Adani [56] and Scaglia [57] used the maximum oxygen uptake rate measured for a short period around the maximum of biological activity.

Concerning stabilization, the respiratory quotient i.e. the ratio of carbon dioxide production to oxygen consumption was investigated as a potential indicator of stabilisation. The respiratory quotient was assumed to depend on biochemical composition of organic material. Its variation was studied by Nakasaki [61] and it was proposed to be used to control the composting process Atkinson [62]. Others found its variation was low which impedes such use [53]. Adani [56] and Scaglia [57] proposed a Dynamic Respirometric Index and considered that compost exhibited a high level of stability when DRI was lower than 500 mg O2/kg OM/h. The European Commission [63] suggested that OURs lower than 1 g O2/kg OM/h can characterize stable composts [64]. Whatever the level proposed to validate stability, the proposal for such an index allows to compare the organic wastes regards to the composting time required to reach the defined threshold. In controlled conditions at laboratory, this time depends mostly on the intrinsic characteristics of the waste. At real scale, it also depends on the composting process i.e. on oxygen supply and air distribution. Thus, in almost all cases, this time should be higher at real scale than in controlled conditions. However, its determination, even in controlled conditions, would help composting operators to adjust their process to the type of waste, especially regarding the aeration strategy and the composting duration. Thus, Komilis [64] defined this time as "a key parameter for the proper design of solid waste composting facilities". However, few papers compare organic wastes according to the aerobic treatment duration required for their stabilization [65].

The biodegradability was also considered regarding its influence on the rise of material temperature during composting. Although most of the models of the composting process associate the heat production to the removal of organic matter or to the oxygen consumption rate [66], literature accounts for only two articles [57, 67] searching for an experimental quantitative correlation between temperature rise and oxygen consumption during composting. As for time required for stabilization, the rise of material temperature does not depend only on waste nature and properties, but also on the composting process and on the size of the composting cell. However, provide a way to estimate the temperature rise could be helpful to formulate composting mixtures even at real scale.

The recent paper by Guanrdia [68] aims to compare household waste, separated pig solids, food waste, pig

slaughterhouse sludge and green algae regarding their biodegradability, their stabilization kinetics and their temperature rise during composting. Three experiments in lab-scale pilots (300 L) were performed for each waste, each one under a constant aeration rate. The aeration rates applied were comprised between 100 and 1100 L/h. The biodegradability of waste was expressed as function of dry matter, organic matter, total carbon and chemical oxygen demand removed, on one hand, and of total oxygen consumption and carbon dioxide production on the other. These different variables were found closely correlated. Time required for stabilization of each waste was determined too. A method to calculate the duration of stabilization in case of limiting oxygen supply was proposed. Carbon and chemical oxygen demand mass balances were established and gaseous emissions as carbon dioxide and methane were given. Finally, the temperature rise was shown to be proportional to the total mass of material biodegraded during composting.

3.4 Ammonia and GHG emissions

As is well known, methane (CH₄) and nitrous oxide (N₂O) are both significant greenhouse gases (GHG). According to the report of International Panel on Climate Change (IPCC), the global warming potential of CH₄ and N₂O, on a 100- year frame, are 25 (CH₄) and 298 (N₂O) times higher than that of carbon dioxide (CO2) respectively [69]. Until 2004, the CH₄ and N₂O account for the global anthropogenic GHG emissions 14.3% and 7.9% separately [69]. Agriculture has been identified as a main source of GHG emissions, about 13.5% of global anthropogenic GHG was emitted from agricultural production [69]. It was estimated that 80% of N₂O and 40% of CH₄ emitted from agriculture activities [70].

In terms of its inexpensive costs and rather simply technique, composting was used widely, especially in developing countries. For example, in China more than 17 million tons organic fertilizer was produced form composting per year; and in the municipal solid waste and sewage sludge treatment field, the proportion of composting increased rapidly. But the emission of harmful gases from composting caused serious environmental problems. As the results of nitrification and denitrification, about 0.02% to 9.9% of total nitrogen (TN) was emitted in the form of N₂O; and caused by the lack of oxygen, 0.1% to12.6% of total organic carbon (TOC) was lost as CH₄ [71, 72, 73, 74, 75, 76, 77]. There is a growing international focus on the GHG emissions from composting [16, 70, 78], especially for windrow system. It was reported that the turning frequency, compact effect, the scale of the pile and the manure characters all could influence the GHG emissions [71, 74, 79, 80].

The effects of C/N ratio, aeration rate and moisture content on the emissions of GHG and ammonia during composting of mixtures of pig faeces and chopped cornstalks were investigated in the study of Jiang [80]. Lower C/N ratio (higher proportion of faeces) caused higher methane emission by reducing the air spaces and increasing the easily available carbon sources. Lower C/N ratio is preferable to increase the NH₃ emission. High aeration rate can reduce the emission of CH₄, whereas the emissions of N₂O and NH₃ increase. Low aeration rates can reduce the NH₃ emission and delay and prolong the ammonification phases. The moisture content can affect the methane and ammonia emission during the composting period, but not significantly. The orthogonal

analysis showed that mixtures with a moisture content of 65%, aeration rate 0.48 L/(kg dm•min) and C/N ratio 21 should acquire the lowest total GHG emission.

3.5 Carbon dioxide production

Composting of agro-waste being a complex process, while developing mathematical models to describe this process, adequate emphasis should be given to both model complexity as well as accuracy of experimental data. Therefore, the focus should be to model the process with key parameters requiring simpler experimentation, capable of giving accurate data. Many mathematical models have been proposed for composting of agro-waste in published literature. Higgins and Walker [81] proposed a model for aerobic organic solid decomposition, with simulations with substrate specific kinetics. The deviations of predicted results from experimentally determined values were attributed to existence of heterogeneous composition of substrate, as against homogenous composition assumed in the model. Briski [82, 83] reported aerobic composting of tobacco solid waste with the objective of stabilizing this waste. The mathematical model was developed with the assumptions that oxygen concentration was practically equal at all the points inside the experimental bioreactor, the compost process was adiabatic, air flow rate was constant, humidity was constant, composting rate was expressed as degradation of the dry substrate, and biodegradation rate was uniform all over the substrate bed. Hamelers [84] has presented a review of approaches for modeling of composting kinetics. It is stated in this work that compost modeling is in general characterized as inductive, data is starting point which determines the type of model used. It is argued that such inductive approach has reached its potential in design and development of optimized compost facilities as per the stringent demands of the latest regulations. Limitations of measurement techniques and magnitude of resources required for collection of experimental data are also major drawbacks of such and Yaldiz approaches. Kulcu [85] reported determination of aeration rate and kinetics of composting of agro-wastes. This study was aimed at determining aeration rate and its kinetics in aerobic composting of mixture of grass trimmings, tomato, pepper and eggplant wastes. Carbon dioxide rate and temperature changes were recorded along with moisture content, pH, and organic matter each day. Komilis [64] carried out kinetic analysis of aerobic solid waste composting of food waste, mixed paper, yard waste, leaves, branches, and grass clippings under optimal conditions. Mineralizable solid carbon was assumed to comprise readily, moderately, and slowly hydrolysable carbon fractions. Progress of composing process was evaluated by measuring carbon dioxide production. Nakayama [86] presented a numerical model of composting process with aeration. Bueno [87] reported that a second order polynomial mode consisting of four independent process variables (time, moisture, aeration, and particle size) was found to accurately describe the composting process. Baptista [88] discussed composting kinetics in full-scale mechanicalbiological treatment plants. The salient characteristics of the model were first-order kinetics, use of correction factor for temperature, use of correction factor for oxygen, correction factor for moisture content, correction factor for free air space, and initial biodegradable volatile solids content.

In the mechanism of aerobic decomposition of agricultural solid waste hydrolysis forms the first stage as a result of which the biodegradable components of solid waste eventually enter into aqueous media. The hydrolysis rate of a particular component depends upon its micro structure defined by binding of cellulose by compounds like hemicelluloses and lignin. The degradation of cellulose by microbes takes place after breaking of the protective layers. Cellulose decomposes to glucose and hemicelluloses to arabinose, mannose, xylose, glucose different types of sugars, alcohols, organic acids like amino acids etc. These products of decomposition of cellulose and hemicelluloses are water soluble and therefore enter the aqueous media during decomposition. A part of carbon delivered to aqueous media after hydrolysis is then converted into carbon dioxide. Remaining carbon is retained by the humus substance, which is the final stabilized produce of biodegradation of organic agro-waste. A schematic presentation of the phenomenon described above is shown in Figures 1 and 2 [89].



Figure 1: Pathway of Carbon during Composting of Agro-Waste



Figure 2: Compost Model for Agro-Waste

Carbon dioxide production during composting of agro-waste can be taken as the indicator of rate, progress and termination of compost phenomenon and stabilization of organic matter, leading to a balanced compromise between complexity of mathematical model and extensive experimentation. Modeling and simulation of composting of agro-wastes based on experimentally measured carbon dioxide production would reduce the experimental effort, time, and other physical resources in design of optimized compost process for disposal of agro-waste. In the study of Tripathi and Srivastava [89] modeling and simulation of composting of a mixture of agro-wastes like sugarcane bagasse, soya husk, wood straw, mixed with food waste is presented. This approach requires estimates of initial values of different carbon fractions. The effect of such estimates on prediction of carbon dioxide production is also studied in this work.

4 MATERIALS AND METHODS

4.1 Composting process

In the present work, composting is studied as a method for the management of Olive Tree Lops (OTLs). The main objective of this study was to understand how the composting process works and to estimate the N and C losses during the procedure. The composting process studied herein is referred to as the "home composting" and it took place in 400 lt plastic buckets. OTLs were used, either on their own or in combination (cocomposting) with grass and seaweeds. More specifically, four mixtures were prepared: C1: OTL; C2: OTL and grass; C3: OTL and seaweeds and C4: OTL. Mixtures C1, C2 and C3 were prepared and studied during the winter period, while C4 was prepared and studied during the summer period, in order to delineate the influence of temperature on the composting process (Fig. 3). It must be noted that the addition of grass into the mixture corrects the C/N ratio to an optimum value of 30:1, thus comprising of an ideal mixture, which consists of two different feedstock materials [90]. On the other hand no specific chemicals -except pigeon dropping (PD) - were used as activators.



Figure 3: Schematic representation and images of the four mixtures for composting; C1: OTL; C2: OTL and grass; C3: OTL and seaweeds and C4: OTL.

The OTLs used were shredded into small pieces (less than 1 cm length) in order to facilitate their degradation (**Fig. 4**). The final goal of this study was to assess the C and N losses, to record how different materials affect these losses and whether the composting period (summerwinter) can affect the C and N balance during composting.

As is well known, the composting process requires adequate conditions for pH, temperature, moisture, oxygenation and nutrients, in order to secure the development-action of the microbial population [91]. A certain period after the process initiation (45 days), it was observed that the compost mass under investigation was appreciably decreased. Thus, the buckets were re-filled by the same mixture in order for the compost temperature to reach the necessary for the process levels.

Operational parameters (temperature, moisture and oxygen levels) were monitored with a frequency of 4-5 days. The frequency of both turning and watering was made by the following protocol:

- If the compost was characterized at least by one of the following characteristics: RH > 90% or T $> 55 \ ^{\circ}C$ or $O_2 < 15\%$ then it was turned in order to achieve the necessary temperature reduction and the proper functioning of the system.
- If RH < 60% then watering was carried out to support the microorganisms viability in the

compost mass and thus, the degradation process.



Figure 4: Experimental composting buckets (a), converting fresh OTL (b) to mature compost (c).

4.2 Compost analysis

During the composting process, among others, the following physicochemical parameters were measured and are reported in the present work:

- Total nitrogen, using the micro-Kjeldahl method [92].
- Total organic carbon, TOC [93].

The chemical analyses of the four composts were made with a two weeks' frequency.

In order to estimate the total C and N quantity at the four buckets, the weight of all materials was recorded both at the beginning and the end of the experiment, when the compost was stable and mature. Additionally, the moisture content of the materials was measured and the weight values were converted into values of dry weight.

5 RESULTS AND DISCUSSION

5.1 Carbon balance

Carbon (C) content was assayed every 15 days. Carbon content was decreased during the composting process and was about 30% for the four final composts (Fig. 5). This organic carbon content value in the final composts is in agreement with other literature results in which its value for final products ranged between 30-50% [52, 92]. The available C was primarily lost as CO_2 during the immobilization process [94].



Figure 5: Evolution in time of TOC for the four different composting experiments

At the experiments of the present study, C and N values were measured from the beginning to the end of the composting process, for a period of about 200 days. The materials which were added to the buckets were rich in both N (grass) and C (OTL) and therefore the C:N ratio was optimum for all mixtures. The results of chemical analysis about the C losses for each bucket separately, are shown at **Table 3**. It should be emphasized that the total carbon losses are given (and not only carbon content decrease) taking into account the overall mass losses.

 Table 3: Total carbon losses at materials of the four buckets.

	Bucket 1	Bucket 2	Bucket 3	Bucket 4
Total initial amount of materials (kg)	23.8	30.6	41.5	32.3
Initial % TOC	50.5	45.1	50.2	49.7
kg C at the initial amount of materials	12.0	13.8	20.8	16.0
Total final amount of materials (kg)	15.0	24.5	22.0	24.2
Final % TOC	28.4	30.9	35.2	28.4
kg C at the final amount of materials	43	7.6	7.7	6.9
C loss (Kg)	7.7	6.2	13.1	9.1
% loss	64.6	45.1	63.0	57.2

It was observed that all materials were characterized by an absolute reduction of C from 45 to 65%. The greatest losses were recorded in buckets 1 and (OTLs and OTLs plus seaweeds, respectively). The smallest loss was recorded at the bucket containing the mixture of OTLs and grass (bucket 2). It's worth noting that the same material (OTLs), showed a similar fluctuation in C values both during the winter and summer experiment, while the total C content in both final composts were completely identical. It was also observed that the high N content of materials (OTL and grass) contributes to the reduction of C losses from the mass of composting materials (**Table 3**). Therefore, lower C losses during the composting process seem to have benefited by the presence of high N content at the studied materials.

It should also be noted that the C content was decreased in all buckets due to the degradation of the materials by micro and macro-organisms. These organisms use C as an energy source for their metabolic activities. Between 55-75% of all plant residues are released into the atmosphere as CO_2 , although there are different rates of release from various organic materials incorporated into the soil. Generally, more C is lost to the atmosphere from the organic substrate; the less C is stabilized in the humus of the final compost. Most of the residual C incorporated into new humus in the form of peptides and polysaccharides. Thus, C loss is due to its removal from the mass of material in the form of CO₂ and CH₄ to the environment. As is well documented, these gases are the major contributors to the greenhouse effect. This questions composting's suitability as an environmentally friendly method for organic residues exploitation.

Gaseous emissions depend on waste nature and on composting conditions and duration. In a review on environmental impacts of biological treatment of organic waste, Mallard [95] reported some ranges of carbon dioxide and methane emissions measured during composting at real scale and in pilot schemes. The emissions of CO₂, expressed as g CO₂/kg DM, were between 110 and 220 for household waste, between 150 and 750 for animal by-products, around 900 for biowaste and between 580 and 760 for wastewater sludge. Mallard [95] also reported a wide range of methane emissions, i.e. between 0 and 11.9 (g CH₄/kg DM), for animal byproducts, and between 0.5 and 9.5 for household waste.

5.2 Nitrogen balance

Nitrogen (N) content was also assayed every 15 days. The highest N content was determined for the OTLs and grass mixture, while the lowest for the OTLs and seaweeds mixture (**Fig. 6**). The total nitrogen content in the final four composts was about 1.5%, an adequate value for their use in organic cultivations. This nitrogen content value coincides well with results of other similar studies, in which the nitrogen value in the final products ranges between 1.2-1.7% d.w. [52, 92].



Figure 6: Evolution in time of N for the four different composting experiments

It should be noted that the majority of N is lost in the form of ammonia, where volatilization accounts for over 92% of all nitrogen losses. The experimental results show that the N losses were much greater than the C losses (N losses between 62 to 76%). The most significant N decrease was observed, as for C, at the buckets 1 and 4

(OTL), while the smallest N loss was recorded for buckets 2 and 3 (grass and seaweeds, respectively). However, the N loss did not show great variation among the four samples (**Table 4**).

 Table 4. Total nitrogen losses at materials of the four buckets.

	Bucket	Bucket	Bucket	Bucket
	1	2	3	4
Total initial amount of materials (kg)	23.8	30.6	41.5	32.3
Initial % N	3.5	3.7	2.4	3.3
kg N at the initial amount of materials	0.8	1.1	1.0	1.1
Total final amount of materials (kg)	15.0	24.5	22.0	24.2
Final % N	1.5	1.7	1.5	1.5
kg N at the final amount of materials	0.2	0.4	0.3	0.4
N loss (Kg)	0.6	0.7	0.7	0.7
% loss	76.0	62.8	70.0	66.3

The N loss is caused by the release, from the compost mass, of gaseous ammonia (NH_4) to the environment. The ammonia is produced by bacteria acting during the phase of decomposition of the organic matter. It is worth mentioning that ammonia emitted from the composting process does not contribute to global warming. In addition to the above, in our experiment N loss was probably also caused by watering the material, as the base of the experimental buckets were in direct contact with the ground.

It is also worth noticing that for the same material (OTLs), but for different composting periods (wintersummer), different N losses were recorded (higher N loss during the winter period).

According to Fukumoto [96] most nitrogen was lost in the form of NH₃, but also a considerable part was lost in the form of N₂O, as in this study the N₂O emissions were various from 1.5% to 7.3% of initial total nitrogen. These results were similar to the research of Szanto [77], but comparatively higher than the results of Wolter [76] and Sommer [97], where only 0.1% to 1.9% of TN were emitted in the form of N2O. Aeration condition was one of the reasons responsible for the difference, in the research of Szanto [77] an effective aeration facility was constructed in the bottom of the composting reactors to enlarge the chimney effect and in the study of Fukumoto [96] a ventilation blower was used to draw out the air in the composting chamber. All these actions accelerated the gaseous emission from the compost piles. Without these aeration actions, even the gaseous concentration in the pile was considerable high, the surface emission was limited [98]. In forced aeration systems the emission rates depends largely on the air flow. It was reported that the size of composting piles could influence the N2O emissions significantly, small piles had higher emission rate than bigger ones [96]. The previous studies showed that low emission rates are always coupled with large pile size [72, 97, 99], and vice versa [77, 96, 100].

In windrow system without forced aeration in the top layer parts aerobic conditions predominate. In these regions a microbial oxidation of CH_4 may be possible. In forced aeration systems fresh air passes through the piles from the bottom to the top, caused the a lower O_2 supply in the top parts. When the CH₄ pass through these regions there were no suitable conditions to oxidation. Coupled with the aeration and small size which were discussed above the methane emission from the aeration system was high. The total GHG ranged from 324 to 743 kg CO₂-eq/ton dm. Orthogonal analysis showed that both aeration rate and C/N ratio could affect the total GHG emission. The treatment with a moisture content of 65% and an aeration rate of 0.48 L/(kg dm·min), and a C/N ratio of 21 should acquire the lowest total GHG emission.

6 CONCLUSIONS

In this study, the total N and C losses during the composting of three different materials (OTLs, grass and seaweeds) were estimated. Continuous monitoring of the experimental buckets for a period of 200 days and the results of various chemical analyses showed that throughout the composting process, both C and N gradually decreased at an absolute basis. The N losses were higher than the C losses for all buckets.

Environmental conditions (winter-summer) significantly affect C and N losses and thus the compost quality.

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10 LOGO SPACE



