Attard, G. (2019). *Xjenza Online*, 7:84–96.

Xjenza Online - Science Journal of the Malta Chamber of Scientists
www.xjenza.org
DOI: 10.7423/XJENZA.2019.2.01

Research Article

A study to define the physicochemical characteristics of biochar from manure generated on 3 different livestock farms in Malta

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Abstract. The amounts of livestock manure produced in Malta surpasses the application rate as stipulated by the Nitrates Directive with the consequence of having an accumulation on farms. In such cases, manure becomes a liability instead of a benefit, incurring significant risk in creating environmental pollution. Pyrolysis of manure is an interesting alternative to land application, as it has the ability to render organic nitrogen into inert nitrogen gas and reduces manure biomass volumes. This technology utilises high temperature, thereby destroying any potential pathogens that may be present in the manure, has the potential of extracting useful energy and generates potentially high value products, e.g. biochar. The functions and application of biochar when used as a soil amendment to improve soil physical, chemical and biological properties depend on its structural and physicochemical properties. Such understanding is crucial for its sustainable use and application. Manure feedstock originating from large ruminant, small ruminant and poultry operations were subjected to a pyrolysis process at 570°C. The starting nitrogen (N) content was repartitioned into inert N_2 (59%), whilst 38% was retained within the biochar structure. The biochar physicochemical properties relating to electrical conductivity (EC) values, the accumulation of zinc and the alkaline nature, render the application of this biochar on Maltese soils challenging. Alternatively, this biochar could be used as a solid fuel to dry the incoming manure biomass, and the resulting ash utilised to extract potassium and phosphorus.

Keywords: Malta, Manure, Biochar, Pyrolysis

Acknowledgements. This research was financed by the Malta Council for Science & Technology for and on behalf of the Foundation for Science and Technology, through the Scheme for the Provision of Proposals aimed at a Holistic Approach to the Sustainable Management of Livestock Manure and Slurry within a Circular Economy Context.

Author Contributions. All authors had equal contribution towards this study. Denise Grima Connell, Oliver Fenech and Francesco Berti provided technical and theoretical support; George Attard and Anthony Gruppetta contributed to the analysis of experimental results and wrote the paper. All authors read and approved the final version.

Conflicts of Interest. The authors declare no conflict of interest.

1 Introduction

Plant agriculture and livestock production follow stoichiometric processes. Nutrient accretion by plants and farm animals to yield food and fibre, depend on the extraction of nutrients from soils that must be replenished on a regular basis to maintain continuous productivity. Traditionally soil fertility was maintained with the incorporation of livestock manure as a source of organic matter and essential nutrients, which contribute towards meeting the crop nutrient requirement and maintain soil integrity. Regions with intensive livestock production generate surplus manure whose application on land will result in the over fertilisation of the agricultural areas risking significant potential negative environmental repercussions. The Maltese livestock sector falls within

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this category, characterised with a very high density of livestock per km^2 of arable land. The current Maltese livestock inventory stands at an estimated 13,000 head of cattle, a 2500 sow farrow to finish swine herd, 15,000 small ruminants, 250,000 laying hens, an annual grow out of 2 million broiler chickens, a rabbit doe population of 15,000 and 4100 equines, while the national total available agricultural area for the application of manure generated by these animals is defined at just 11,000 hectares. To mitigate the risk of over application of manure the EU has implemented regulations to safeguard the environment, of which European Commission (1991) is the most important. This directive sets the limits for the application rate of livestock manure, expressed as the amount of nitrogen per hectare of land, established at a maximum of 170 kg of N per hectare. The livestock industry is showing a declining trend, mostly due to improvements in milk yields per cow in the case of dairy cows and to market forces and competitiveness in all the other sectors.

Given the limited agricultural land base available on which grain, fodder and roughage can be cultivated, diet formulations by local feed mills are by default totally dependent on the importation of cereals purchased on global markets. The excreted nutrients resulting from these feeds, with special reference to nitrogen, now in the form of animal manure are in excess to what can be applied to land. The growing concern about environmental consequences of excessive fertilisation from animal manure necessitates the implementation of alternative options. Techniques such as digestion (anaerobic and aerobic) and composting that have a proven track record, especially in Northern Europe, have been proposed to address the challenge of manure accumulation on farms. However, under local conditions, all these techniques have shown some form of limitation. In some cases, these techniques just serve to shift the challenge of the sustainable management of manure up to the next tier without having reached any tangible reduction in nutrients associated with over fertilisation and environmental pollution.

A potentially interesting alternative is the thermochemical conversion of manure into biochar by using pyrolysis (Cantrell et al., 2012). This technology has added benefits such as: a shorter conversion time compared to composting, the absence of non-biodegradable and toxic substances, high processing temperatures that are adequate to neutralise all pathogens potentially found in manure, and the conversion into value-added products (Ro et al., 2010).

The potential processing of manure through pyrolysis with the subsequent recycling of biochar has major advantages over land application:

(i) the energy content of the biomass is capitalised as renewable energy;
(ii) the nitrogen content is mainly transformed into inert N_2;
(iii) more valuable components, e.g. phosphate and potassium, are retained in the solid fraction which is dry, odourless and easy to handle.

The functions and application of biochar when used as a soil amendment to improve soil physical, chemical and biological properties depend on its structural and physicochemical properties Angin et al. (2014). Such understanding is therefore crucial for the sustainable use and application of the biochar.

This study evaluates the physicochemical properties of manure produced by the poultry, cattle and sheep sectors on the Maltese Islands and the resulting biochar generated from this manure biomass feedstock during the pyrolysis process.

2 Materials and Methods

2.1 Farm Selection

The recorded history always makes reference to the fact that Malta does not produce enough grain to meet the needs of its inhabitants let alone to meet the nutritional requirements of the resident livestock. One can safely affirm that this situation is very much the same today as it was back then. National Statistics Office, Malta (2016) states that only 5,290 hectares of arable land are dedicated to the cultivation of livestock fodder, mostly in the form of roughage, such as winter wheat, barley and other similar crops. The harvest meets an estimated 10% of the nutritional needs of the ruminant sector. Hence, the remaining 90% required by the ruminant sector, together with all of the nutritional requirements to feed the monogastric livestock, has to be imported. The grain is procured, normally through international tendering procedures stipulating nutrient limits that have to be met. Due to reasons of economies of scale, the local feed mills act together as a consortium for the procurement of feed grade cereals which are then distributed according to the respective feed mill's market share.

This study assumes that the different herds within the respective livestock sectors do not exhibit significant differences due to feed, animal breed or manure management. Given that:

(1) feed grade grain, irrespective of the feed mill, all originates from the same source;
(2) the fact that there is minimal breed variability amongst herds (cattle are mostly Dutch Frisian, while sheep belong to the local Maltese type);
(3) poultry: most egg layers are imported from a single source as pullets at point of lay, while broilers are supplied from one local hatchery;
(4) manure management is regulated by Justice Ser-

vices of Malta (2007), that provides for the uniform management of manure across the various livestock sectors;

In the opinion of the authors, the selected farms are a true representation of the various sectors.

2.2 Manure Biomass Feedstock

Selection of manure types for analysis was based on the quantity of manure generated by the different livestock sectors in Malta. Previous survey results in E-cubed consultants, Adi Associates (2015) were used to identify the main contributors to the generation of manure on Malta and Gozo. Sampling was performed in accordance to the relevant and adapted guiding standards of ISO 18400 series. Following collection, the 50 kg samples were packaged in 60 L drums and shipped under refrigerated conditions (+4°C) to Environlab s.r.l. in Italy for analysis.

2.3 Daily Manure

The selected dairy farm is situated to the North-East side of the island within the Magħtab basin. This dairy unit is affiliated with the only Dairy Cooperative (Kooperattiva Produtturi tal-Ħalib) and sources its concentrate feeds from the same coop feed mill. Roughage is mainly alfalfa hay in bales of around 700 kg imported from Spain, which is procured through private importers or through the cooperative itself. The locally produced wheat crop is directly purchased as whole crop bales including straw and ears of grain. The unit houses 412 heads of cattle, of which 221 are females over 2 years.

On average, each milking cow is fed a ration of 13 kg of Special KPH Dairy Pellet Concentrate, 6 kg of Maltese whole crop wheat, 7 kg of alfalfa hay with 1 kg of sugar beet and additional minerals and vitamins, all blended together in a TMR (Total Mixed Ration) mixer and distributor. The remaining herd made up of dry cows, pregnant heifers, young heifers and bulls receive a ration of 5 kg of Standard KPH Dairy Pellet Rations and 5 kg of Maltese whole crop wheat.

The milking herd is kept in a large shed and their excretions are scraped away every 12 to 24 hours and are processed through a drum filter separator (model ROTA 2000). The solid fraction is collected in a manure clamp. The rest of the herd is kept on a dry bed system and the bedding is removed circa three times per year and replaced with fresh bedding. The bedding is mainly low-grade straw but may vary from time to time to include wood shavings, sawdust and shredded paper. The litter is scraped away by a mechanical shovel and deposited in the manure clamp present on farm.

Grab samples were randomly collected from various parts of the manure in the clamp and pooled together to make up a 50 kg manure sample. The "as received" moisture content was measured at 56.4%.

2.4 Sheep Manure

The selected unit is situated in the central part of Malta and holds a herd of 302 heads, of which 193 are milking ewes.

The daily ration on this holding includes 800 g of normal sheep pelleted feed supplied by Andrews Feeds Ltd and about 1 kg of Maltese whole crop wheat per head. The milking ewes also receive 1 kg of Andrews Sheep Lactation Pellets, whilst being milked in the parlour.

All animals are housed in sheds on a deep litter system. The manure/bedding matrix is made up of chaff and straw when chaff is no longer available together with the accumulated manure and urine. Fresh bedding is added as necessary to maintain the flock in a dry and clean condition. The litter is scraped away by a mechanical shovel once a year and deposited in heaps in fields adjoining the farm.

Random grab samples were pooled to make up a 50 kg sample of sheep manure collected from this holding directly from the heaps. The "as received" moisture content was determined to be 59.2%.

2.5 Poultry Manure

Poultry manure was sourced from two adjacent farms, one being an egg laying unit and the other a broiler operation, both found in the Maghtab basin. Samples from both farms were pooled to make up the representative sample of poultry manure.

The broiler operation has a capacity of 18,000 chicks kept in different sheds. The different sheds carry multi age flocks with a rotation of sheds for slaughter. The grow out cycle is of six weeks after which broilers are shipped out for processing. The feeding regime consists of three different types of concentrate rations, chick crumbs followed by chick starter switching to a standard finisher rations in the last 3 weeks of the growing cycle. All feeds are formulated and compounded at an adjacent feed mill (MCP). The applied bedding is always imported wood shavings. The empty sheds are scraped clean from the litter by means of a mechanical shovel; they are cleaned, washed and disinfected after every cycle. The broiler litter is stored in a manure clamp.

The layer unit has a flock capacity of 40,000 heads. Laying hens are housed in different sheds in cages that are 5 tier high. The feeding regime consists of a standard poultry layer ration in a granulated form produced by Andrews Ltd feed mill. Cages are equipped with manure mats, and sheds are emptied twice a week. Manure is scraped off the mechanical mats and stored in the manure clamp present on farm.

Manure from the broiler farm was two days old, whilst that from the layer farm was collected straight after being deposited in the manure storage area. The pooled

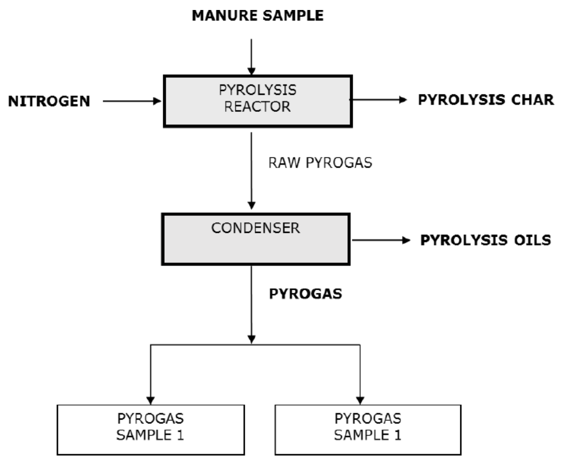

Figure 1: Schematic diagram of the pyrolysis process used for this study to produce for producing char (biochar), oils (bio-oil) and pyrogas (syngas).

poultry litter had an "as received" moisture content of 57.6%.

2.6 Preparation

Upon receipt of the samples at the laboratory, representative samples from the "as received" manures were prepared by pooling three sub-samples of 2 kg/each, taken from different parts of the received manure sample of 50 kg. Half of the total weight of each manure sample was dried further in an oven at 105°C to reduce its water content before initiation of the pyrolysis procedure.

2.7 Pyrolysis system and process

The manure samples were subjected to pyrolysis by means of a pilot test rig consisting of a furnace (reactor), a stack and a bio-oil condenser, as shown in **??**. For each type of manure, a "blank" test was performed to record the evolution of its transformation in time and to calibrate the test rig by using the Flame Ionization Detector (FID) analyser data and the acquisition system for the monitoring of gas flow evolution.

Each manure type was separately tested in a pyrolysis test reactor, which was filled with a weighted amount of dried manure of about 500 g and then put in the preheated oven at 650°C. The temperature during the test was maintained at 570°C. A three litre/min nitrogen flow, controlled by means of a gas flow meter directly connected to the nitrogen gas cylinder, was connected to the pyrolysis reactor as a carrier for the evolving chemical species created by the pyrolysis reaction. The gas flow was sent through a water chilled (4°C) spiral condenser with a collecting bottle for condensed tar. This was followed by two gas bubblers (each filled with 3000 mL of water) leading to the gas sampling line coupling a connection for three litre gas cylinder sampler, two activated carbon cartridges and an on-line gas flow FID analyser used to monitor and record the pyrolysis syngas flow evolution in time.

During each test, a gas cylinder sample was taken at gas flow peak production, while the two activated carbon cartridges were left connected up to the test end. At the end of each test, the biochar residue left in the pyrolysis reactor was weighed and fully characterised.

2.8 Feedstock and biochar analysis

Both the feedstock and biochar were tested in an ISO 17025:2005 accredited laboratory, Environlab S.r.l., with accreditation no. 1298. Standard analytical procedures were used and, in the absence of a standard method, inter-laboratory SOPs (Standard Operating Procedures) were utilised. The feedstock material was characterised as received, whilst biochar was collected following each pyrolysis test carried out on individual manure types. Both feedstock and biochar samples were digested for subsequent determination of Sb, As, Ba, Be, Cd, Cr (III), Hg, Ni, Pb, Cu, Se, Sn, Tl, Te, Zn through UNI EN 13657:2004. The concentration of parameters was determined by ICP-OES (Inductively Coupled Plasma - Optical Emission Spectrometry) through standard method UNI EN ISO 11885:2009. Hexavalent Chromium was quantified through method CNR IRSA 16Q 64 Vol 3 1986. Total Organic carbon was analysed by means of standard method UNI EN 13137:2002, whilst hydrocarbon content in the range of C10 to C40 was determined by gas chromatography through UNI EN 14039:2005 + EPA 5021A:2014 + EPA 8015C:2007. UNI EN 15407:2011 was utilised as a method to determine the C, H and N content for elemental analysis. The calorific value was determined through UNI EN 15400:2011. CNR IRSA 1 Q 64 Vol 3 1985 was utilised for the determination of pH. Dry weight (at 105°C) and residue on ignition (at 600°C) were determined through UNI EN 14346:2007 (Method A) and CNR IRSA 2 Q 64 Vol 2 1984, respectively. Analytical results were compared with limits set by the Italian Legislative Decree no. 75 of 29 April 2010 "*Re-organization and revision of the discipline regarding fertilisers, in accordance with Article 13 of Law no. 88 of 7 July 2009*". This Decree is the transposition in the Italian law of European Regulations: Regulation (EC) No 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilisers; Council Regulation (EC) No 834/2007 of 28 June 2007 on organic production and labelling of organic products and repealing Regulation (EEC) No 2092/91; Commission Regulation (EC) No 889/2008 of 5 September 2008, laying down detailed rules for the implementation of Council Regulation (EC) No 834/2007 on organic production and labelling of organic products with regard to organic production, labelling and control.

Biochar has been included in the Italian Decree no. 75

T (°C)	Reaction
100–120	drying
250	de-oxidation, desulfurisation
340	aliphatic bond breakage
380	biochar formation
400	breakage of C-O and C-H bonds
400–600	tar formation

Table 1: Chemical reactions that occur at the different temperatures throughout the pyrolysis process.

of 29 April 2010, in an update of Annex 2 - Soil conditioners published in Ufficio Pubblicazione Leggi e Decreti (2010).

3 Results and Discussion

The most common ways to extract energy from manure biomass involving thermal process are combustion, gasification and pyrolysis. During the combustion process, the biomass is completely oxidised and converted to heat steam and carbon dioxide. This process is generally associated with environmental pollution issues. The gasification process involves a procedure partly oxidising the biomass, whilst converting the solid fuel to gas. Pyrolysis involves the heating of the biomass in the absence of oxygen. Jahirul et al. (2012) give an extensive technological review on biofuels production through biomass pyrolysis. The process of biomass pyrolysis is very complex, consisting of simultaneous and successive reactions, when heated in an oxygen free environment. The thermal decomposition of organic components commences at 350–550°C and goes up to 700–800°C. Table 1 shows the different chemical reactions happening during pyrolysis at the different temperatures throughout the process. Compounds with long chains of carbon, hydrogen and oxygen break down into smaller molecules, resulting in the production of solid biochar, gases and vapours, that at ambient temperature condense to a dark brown viscous liquid also known as tar/bio-oil. The end product yield is directly related to the conditions of the process, amongst which there are the type of feedstock and its moisture content.

3.1 Pyrolysis and the Nitrogen cycle

Animal dung is used to be incorporated into soil to improve and maintain its fertility, but excessive application of manure can lead to serious issues in soil eutrophication, high salt content causing plant toxicity and greenhouse gas emissions (Dagnall et al., 2000; Zhange et al., 2011). Alternatively, it can be considered as a type of renewable energy feedstock when processed through pyrolysis.

In general, the results of this pyrolysis study, agree with those reported by Meesuk et al. (2013), in that the majority of nitrogen in the initial manure biomass was converted into N2 above 500°C. This study indicates that at a temperature of 570°C, of the initial N content present in the original biomass, 59% was released as inert N_2, 38% was retained within the biochar structure, 2% released as NO and 1% as N_2O. The bulk of the organic nitrogen found in animal manure is in the form of proteins, lipids and polysaccharides (Meesuk et al., 2013), that can potentially be converted into NO_x and N_2O during the pyrolysis process (Thomas, 1997; Tsubouchi et al., 2008; Wojtowicz et al., 1993). The partitioning and transformation of nitrogen into tar/bio-oil, syngas and biochar is a key factor in limiting the formation of NO_x and N_2O. The schematic representation showing the N-reduction from biomass and its subsequent portioning during the pyrolysis process is presented in figure 2.

3.2 Physicochemical characteristics of manure feedstocks

The results of the different parameters performed on the feedstock are presented in table 2. When "as received" samples of the biomass were analysed to determine the dry matter content, all proved to be relatively wet, as they all contained less than 50% dry matter. This high moisture content is due to the fact that at time of collection the manure had not undergone the necessary time period to cure and go through a process or air drying. Given the relatively dry climate, also during the rainy season, biomass stored in a proper design clamp that allow cross ventilation will undergo a process of natural drying and hence result in higher dry matter content. The amount of "wetness" of the biomass has an adverse effect on the pyrolysis process and on the heating value of pyrolysis bio-oil. Quiroga et al. (2010) reported that on average when poultry manure samples were tested for Heating Values, the energy content on the dry matter basis was on average 4.8 times higher than that obtained from the wet manure, due to the amount of moisture present in the wet form. The high moisture content in feedstock is not desirable, as it will cause a lowering in the operating temperature causing inefficiency of the pyrolysis performance. The amount of energy needed to pyrolyse manure can be divided into drying and sensible heat to raise the dried biomass feedstock to the correct pyrolysis temperature; in this case 570°C. The energy required to dry the feedstock is equal to the amount of heat required to raise the temperature of the wet biomass to 100°C plus the latent heat of vaporisation to remove the water and dry the substrate. In general, a proper pyrolysis process requires a feedstock having a moisture content between 5 to 15 wt%, hence the pre-handling of manure in such a way that it undergoes a thorough drying process to reduce its water content can have significant effects on the operating efficiency for

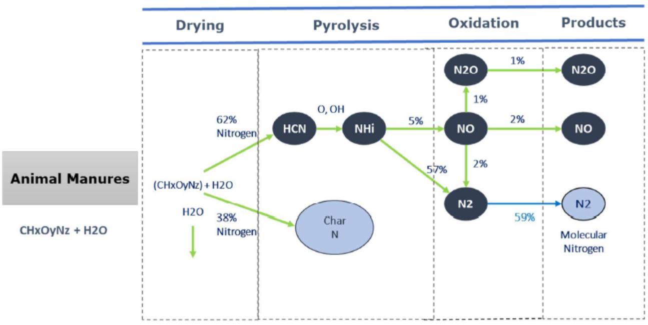

Figure 2: Pyrolytic Denitrification Scheme (HCN: Hydrocyanic acid, NHi: the many and different species which contain one NH chemical group as part of their chemical structure, N_2O: Nitrous oxide, NO: Nitrogen monoxide, N_2: Nitrogen gas).

energy extraction.

The results of the physicochemical analysis on the manure biomass stock show differences inferring that the yield will differ according to type. Table 3 presents differences to the pyrolysis process of different manure types. The table indicates that the three tested samples showed different behaviour, both in terms of final products and in the dynamics of their chemical transformations.

3.3 Physicochemical characteristics of biochar

The analytical results of the feedstocks and biochar are in general in agreement with those published in literature (Antal Jr. et al., 2003; Bourke et al., 2007; Keiluweit et al., 2010) in that the resulting biochar harbours a concentration of stable carbon following the removal of volatile matter. The distribution pattern of the products varied according to feedstock type. The sheep manure, composed of faeces that in part contain undigested fibres and urine is continuously added on to the bedding, generally straw in a deep litter barn design. The deep litter is removed on a yearly basis, thus providing an appropriate environment and allowing sufficient length of time for manure and litter to undergo a decomposition process. The cow manure is composed of faeces predominantly containing indigestible fibres of lignin and segregated into a solid fraction following on farm slurry dewatering. In the case of poultry, which is composed of a 50/50 mix of layer hen manure and broiler litter, the lignin fraction would only be present in the broiler litter as wood shavings. The ratio of biochar: bio-oil: syngas released by poultry manure, cow manure and sheep manure was $1:1:1$, $1:0.5:1.5$ and $1:4:1.7$, respectively. This confirms that the different feedstocks are composed of different complexes that have different boiling points. Hence, depending on the respective boiling points, the volatiles released will segregate according to the respective molecular properties into syngas or condense into the liquid bio-oil. Yang et al. (2006) describe the decomposition rate of individual biomass components with pyrolysis temperature; in that hemicellulose is the first to undergo a decomposition peak at about 300°C, followed by cellulose that peaks at about 400°C, while lignin persists with no evident decomposition peak at 500°C. Hence the resulting biochar recovery is highly related to the amount of lignin lattice present in the original feedstock.

The ash content of biochar differed according to feedstocks, with poultry > cow > sheep. This ranking could be assumed to be the combined effect of premix inclusion in diet formulation and the digestive / absorptive efficiency of the various nutrients found in the respective premix. The Electrical Conductivity (EC) values of the biochars from the different feedstocks were also characterised. This reading is a direct indication on the amount of salts present, which can potentially have undesirable effects on soils. The EC values varied from 40,300 to 29,600 μS cm^{-1}. Cantrell et al. (2012) conducted a regression correlation analysis on the relationship between EC and ash content, concentrations of K, Na and (K + Na) and found an extremely low correlation (R^2 between < 0.005 and 0.13) between % ash and EC, implying that some ash components are insoluble and are incapable of conducting electricity. In contrast, a strong correlation was achieved when EC values were regressed against the concentrations of K, Na and (K + Na) in biochar. In fact, the combined (K + Na) resulted in being the best predictor for biochar EC values. This relationship is of particular significance in the case of Maltese livestock farms, in that most of these farms utilise brackish grown water as potable and/or washing water. This would obviously contribute to increase the salt load in the manures and contribute towards increasing the EC values. Biochar produced from cow manure had the highest EC value among all examined types. Usually the biochar from poultry manure is typically high in EC-influencing elements, generally due to the incomplete assimilation of nutrients by poultry. The higher EC value registered by biochar from cow manure may be due to elements that are exterior to salt content in feed and potable water and the digestive / absorptive capacity of the animal. Often enough, brackish ground water is utilised to wash milking parlours, and the resulting dirty wash water, together with any chemicals that are utilised in the process, being discharged into the manure holding cess pits, thus serving as an additional exogenous source of elements that contribute to additional electrical activity.

In all types of feedstock, the pyrolysis process produced very alkaline biochar (pH > 7), ranging from 11.8 to 12.7; these values are somewhat higher from what is reported by Cantrell et al. (2012) and Singh et al.

Parameters	Sheep	Cow	Poultry
Dry matter content (%)	40.8	43.6	42.4
Moisture content (%)	59.2	56.4	57.6
Lower Heating Value (kJ/kg)	4419	5495	4267
Carbon (% dm)	39.2	42	37.8
Nitrogen (% dm)	1.7	1.2	1.3
Hydrogen (% dm)	6	6	6
Oxygen (% dm)	27.5	44.7	28.5
Chlorine (post-combustion) % w/w	0.38	0.51	0.25
Sulphur (post-combustion) % w/w	0.15	0.17	0.09
Antimony (mg/kg)	<1.25	<1.25	<1.25
Arsenic (mg/kg)	<5	<5	<5
Barium (mg/kg)	15.2	9	11.8
Beryllium (mg/kg)	<1	<1	<1
Cadmium (mg/kg)	<0.25	<0.25	<0.25
Cobalt (mg/kg)	<5	<5	<5
Chromium (mg/kg)	<5	<5	<5
Chromium (VI) (mg/kg)	<1	<1	<1
Mercury (mg/kg)	<0.5	<0.5	<0.5
Nickel (mg/kg)	<5	<5	<5
Lead (mg/kg)	<5	<5	<5
Copper (mg/kg)	7.7	9.4	18.2
Copper (soluble) (mg/kg)	<10	<10	<10
Selenium (mg/kg)	<1.25	<1.25	<1.25
Tin (mg/kg)	1.4	<0.5	0.82
Thallium (mg/kg)	<1.25	<1.25	<1.25
Tellurium (mg/kg)	<1.25	<1.25	<1.25
Zinc (mg/kg)	80.5	26.2	120

Table 2: Analytical results of the different parameters performed on the manure feedstocks.

Observations	Chicken manure	Cow manure	Sheep manure
Pyrolysis products distribution	Syngas 30% Bio-oil 36% Biochar 34%	Syngas 51% Bio-oil 15% Biochar 34%	Syngas 26% Bio-oil 59% Biochar 15%
Reaction behaviour	Syngas production is high, long lasting and stable from its start to its end. No gas production peaks detected.	Syngas production start is fast, it is short lasting and suddenly falls coming to its end. No gas production peaks detected.	Syngas production is slow, long lasting and quite stable from its start to its end. No gas production peaks detected.
Contaminants requiring special attention	None	None	None
Other observations	Zinc content in the biochar is quite high. More analytical tests should be carried out to confirm this value, and a Zinc balance inside the farm's perimeter is to be carried out to suggest possible changes in the current feeding practice to potentially reduce Zinc content.	Zinc content in the biochar is quite high. More analytical tests should be carried out to confirm this value, and a Zinc balance inside the farm's perimeter is to be carried out to suggest possible changes in the current feeding practice to potentially reduce Zinc content.	None

Table 3: Behaviour of the different solid manures during the pyrolysis process

Parameter	Units	Poultry mix	Sheep	Cattle	Italian Fertilisers Decree limit values
Carbon	% of total dry mass	26.3	51.9	43.2	
	Class 1				>60
	Class 2		×	×	>30 and ⩽60
	Class 3	×			>20 and ⩽30
Hydrogen : Carbon (H:C)	Molar ratio	0.022	0.023	0.03	0.7
Total ash	% of total dry mass	55.4	34	44.5	
	Class 1				<10
	Class 2		×		>10 and ⩽40
	Class 3	×		×	>40 and ⩽60
pH value	pH scale	12.7	11.8	12.4	04/12/20
Electrical Conductivity	μS cm^{-1}	31100	29600	40300	1000000
Cadmium	mg/kg	<0.25	<0.25	<0.25	1.5
Copper	mg/kg	89	98.3	40	230
Lead	mg/kg	6.1	8.2	5.6	140
Mercury	mg/kg	<0.5	<0.5	<0.5	1.5
Nickel	mg/kg	10.1	7.2	5.4	100
Zinc	mg/kg	771	299	586	500
Chromium VI	mg/kg	<0.5	<0.5	<0.5	0.5

Table 4: Parameters of interest within the biochar generated from bovine, sheep and poultry manure, compared to limit values set in Italian Legislation

(2010) but similar to results obtained by Zhao et al. (2017). Yuan et al. (2011) reported the very strong positively correlation ($R^2 = 0.97$) between pH values and ash content of biochar, hence probably the main cause of each biochar's inherent alkaline pH is due to the minerals involved in the formation of carbonates such as $CaCO_3$ and $MgCO_3$ and the presence of inorganic alkalis such as K and Na. Biochar having high alkaline pH-values has been associated with potential negative consequences on the soil chemistry of low-buffer capacity sandy soils Novak et al. (2009).

In general, pyrolysis tended to concentrate the mineral and heavy metals within the resulting biochar. The concentration profile of the individual components when compared to the raw feedstock manure did not remain constant. Differences in the metal content of the different manure types may be attributed to the specific husbandry practices and to the particular feed provided for each animal type. The concentration of the elements in the feedstock and biochar was in general lower than the listed ceiling concentrations established by the Italian Legislative Decree of the 29 April 2010, no. 75, on fertilisers. The exceptions were cattle and poultry biochar one, that both showed high concentrations of zinc, that goes beyond the acceptable limits. Although animal feeds are regulated, Zn together with or in replacement of Cu is sometimes included in diet formulations. Cantrell et al. (2012) argues that, while the concentration of some heavy metals in biochar decreases with increased temperature, in the case of lead, zinc and copper this was not so; inferring that they are highly stable elements and not prone to volatilisation during the pyrolysis process. The results from this study tend to be in agreement with those reported by Cantrell et al. (2012).

The variations in EC and the level of Zn present in the biochar from the various manure types indicate that, while there may be uniformity in grain procurement and manure handling protocol across livestock farms, there may be situations on particular farms that will contribute to alter the expected physiochemical parameters. Practices such as the use of brackish ground water in lieu of potable water and or wash water, the storing of reverse osmosis reject brine in the slurry pits and the use of different premixes by the feed mills will all have measurable effects on the contents of the stored manure and hence in the resulting biochar.

3.4 Recovery

In agreement with results reported in the reviewed literature, this study reports that biochar recovery is positively correlated to ash content but negatively correlated to the manure biomass feedstock volatile matter and nitrogen contents. Volatile matter is released by the feedstock during the pyrolysis process: the more volatile released, the higher are the losses resulting in a lower biochar recovery. Likewise, but in an opposite manner, a high ash concentration results in higher biochar recovery. The sheep feedstock, which had the highest release of syngas and bio-oil and lowest ash content, generated the lowest biochar recovery of 15 wt.% db. Although sheep manure generates the least amount of biochar, on the other hand it appears to be most energy dense when evaluated on the basis of the higher carbon and lowest ash contents. Of particular interest, biochar from poultry manure had the highest ash and the lowest carbon content, correlating well with the literature, that generally classifies poultry biochar as having a poor high heating value. Due to the high ash content, manure biochar may be not viable as a commercial fuel.

Similar to the trend in biochar mass recovery when compared to the original feedstock, carbon recovery also decreased. Changes in carbon content occur simultaneously with losses in hydrogen and oxygen (Antal Jr. et al., 2003). Contrary to trends reported by Cantrell et al. (2012), this study indicates that cow manure generated the most stable carbon that did not decompose following thermal treatment. Lang et al. (2005) noted that higher carbon recovery was obtained from manure-based biochar when compared to pyrolysed lignocellulosic feedstocks, leading Keiluweit et al. (2010) to conclude that pyrolysing manure feedstocks releases less volatile carbon when compared to pyrolysing grasses and wood. Cantrell et al. (2012) justified this observation by arguing that manures had a higher propensity to retain carbon following pyrolysis, due to protective mechanisms involving various inherent metals, that change the bond dissociation energies of inorganic and organic carbon. This mechanism was later supported by White et al. (2011), who showed that treating lignocellulosic biomass with inorganic salt solutions altered reaction pathways, resulting in an increased production of biochar. Nonetheless, one has to factor in the effect of digestive processes when analysing manure and more specifically manure from ruminant animals. The digestive physiological process of ruminant animals involves mechanical breakdown, microbial action and enzymatic activity, all coming together to extract the available cellulose and hemicellulose from the consumed roughage. Thus, manure from ruminant animals will contain plant components that have undergone the full digestive process and resisted breakdown, such as lignin. Xu et al. (2013) suggest that biochar yield has a strong positive correlation with amounts of lignin and mineral content of the feedstock.

Poultry manure yielded the lowest carbon recovery. Commercial poultry flocks are given feed containing a corn - soy bean combination with the inclusion of premix containing vitamins and minerals to formulate diets to meet the specific requirements of the flock. Given that the dietary need of poultry does not require complex fibre, feed is usually formulated to contain minimal amounts of lignin. It so follows that poultry manure will be void of lignin, thereby reflecting in the poor ability of retaining stable carbon following pyrolysis. The poultry manure in this study contained a 50/50 blend of cage layer manure and broiler litter. Hence although the poultry excreta have insignificant levels of lignin, the wood shavings used as bedding in the broiler litter is predominantly lignin, which will contribute towards the recovery of stable carbon.

Table 3 shows that cow feedstock generated the highest amount of syngas and the least amount of bio-oil, while the sheep feedstock behaved in an opposite manner, releasing the highest amount of bio-oil and the least amount of syngas.

3.5 Implications for Environmental and Agronomic Management

Maltese Soil Information System (2004) led to the creation of an electronic map of soil properties, with observation points located on a 1 km^2 grid across Maltese archipelago. The outcomes of this project highlighted the following issues that are pertinent to this study:

(1) 58% of Maltese soils have low or very low soil organic carbon content (< 20 g/kg);
(2) soils are slightly and moderately alkaline (pH between 7.3 and 8.5);
(3) 77% of soils are either loamy, clay loam or clay soils, and have clay content higher than 48%;
(4) heavy metal hot spots have been identified, predominantly in the South of Malta;
(5) soils are non-saline (EC 347 $\mu S\,cm^{-1}$); however, in irrigated soils the EC is double (695 $\mu S\,cm^{-1}$).

Lehmann (2007) suggested that when applied to soil, biochar having a carbon-rich lattice can be used as an effective C sequestration agent, when its H:C ratio is less than 0.6. Results indicate that biochar from all the different manure feedstock types had a H:C ratio of 0.022–0.03, thus exhibiting a high C sequestration potential, representing an efficient technique for mitigating against greenhouse gas emissions, while also serving as a carbon source to improve the low soil carbon content. The pyrolysis process concentrates minerals that are essential for plant growth such as Potassium, Phosphorus and Sodium, implying that manure-based biochar may be suited for application as an alternative fertiliser. With respect to heavy metal concentrations in biochar, the higher majority fall within the acceptable limits as stipulated by the Italian legislation and would have minimal impact on increasing soil heavy metal concentrations in a singular short-term application. The suitability of biochar as a soil amendment would depend on feedstock selection, initial nutrient concentrations and the resulting nutrient plant availability status. However, the results show EC values of 29,600 to 40,300 $\mu S\ cm^{-1}$, indicating the presence of high levels of salts, which can potentially contribute to increasing soil salinity. In addition, there is the risk of accumulating some individual heavy metals, in particular zinc, that are at high levels both in manure and in the resulting biochar. The alkaline nature of biochar may be of critical concern when applied to Maltese arid soils, due to its high salinity and alkaline nature. These physicochemical properties render the application on Maltese soils of biochar generated from local livestock manure questionable. Further studies need to be undertaken to determine the suitability of manure biochar application onto Maltese soils.

4 Conclusions

The need to treat animal manure is driven mainly by the requirements of the Nitrates Directive. Livestock manure in Malta is produced from several sources: cattle, swine, poultry, sheep, rabbits and horses, generating significant amounts of manure and litter. These units do not have the capacity to utilise these materials on site and the quantities generated surpass the application rate to the available arable land as stipulated by the Nitrates Directive. In such cases, manure becomes a liability instead of a benefit, incurring significant risk due to:

(1) need for storage of vast volumes of slurry/manure;
(2) creating environmental pollution and animal health risks, due to the accumulation of manure on farms;
(3) risk due to nutrient concentration and potential nutrient escape causing environmental pollution;
(4) issue of economies of scale in applying a technical solution.

Pyrolysis converts nitrogen into an inert gas and reduces volumes. The thermochemical technology employed in the process utilises high temperature, thereby destroying any potential pathogen that may be present in the manures. Pyrolysis has the potential of extracting useful energy and generates potentially high value products. Lima et al. (2009) claim that: “Chars are normally produced to reduce the volume and mass of a particular feedstock and provide a soil amender that improves the physical and nutritive properties through its ash content of hard, compact soils with a high clay content or highly porous soils with a high silica or sand content.” The results show that the biochar produced in this study may not be suitable for use on Maltese soils. The outcomes from this first attempt to define the physiochemical properties of manure and the resulting biochar indicate that further studies involving larger sample size per livestock type are required to verify the physicochemical variations and similarities, in particular the presence of high levels of zinc and EC. Nonetheless, pyrolysis of livestock manures is an interesting substitute to direct land application or incineration. In fact, manure biochar could be potentially used as a fuel to dry the feedstock and the resulting biochar ash can be utilised for the extraction of valuable essential plant nutrients such as potassium and phosphorus. A further economic study on this option will establish the feasibility of the operation.

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