

NoAW project



Innovative approaches to turn agricultural waste into ecological and economic assets

D1.1

Key indicators and methodologies for assessing the impacts on soil, water, air quality and human safety of agro-waste management

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1. Document Info

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Dissemination Level	
PU Public	PU
CI Classified, as referred to Commission Decision 2001/844/EC	
CO Confidential, only for members of the consortium (including the Commission Services)	

2. Summary

<p>Background</p>	<p>The NoAW “No Agricultural Wastes” project will develop an advanced chemical and biotechnological platform to convert a large set of solid assets (wheat straw, winery wastes) as well as manure. Nonetheless, one major challenge of these new waste valorization routes is to obtain better sustainability compared to traditional conversion routes. Thus besides to evaluate the economical sustainability of these innovative wastes management conversion processes, it is of prime interest to assess also the environmental and human sustainability. Such objective and methodologies used have been developed through the Task 1.5: “Harmonizing key indicators and methodologies for assessing the impacts of waste management on soil, water, air quality and human safety”.</p>
<p>Objective</p>	<p>The evaluation of the environmental and human impact need the development of appropriate indicators that could assess it. This work has been realized through the task 1.5 during which:</p> <ul style="list-style-type: none"> ➤ Key sustainability indicators (i.e. environmental, human) for assessing the environmental and human impact of the agricultural wastes management routes have been selected. ➤ Methodologies have been determined that will be used to quantify or evaluate the indicators.
<p>Methods</p>	<p>The key indicators selection for assessing the environmental and human impact of the various wastes management processes have been established by the various partner involved in the task 1.5: APESA, UNIROMA, CBHU, VERMICOM, UM. The definitions of the methodologies that will be further used for quantifying these indicators have been determined according to protocols from partners involved in WP3 and WP4 (i.e. WP in which the wastes management conversion processes will be carried out).</p>
<p>Results & implications</p>	<p>The main results of the deliverables 1.1 are the following ones:</p> <ul style="list-style-type: none"> ➤ Several sustainability indicators have been developed to assess the impact on environment on the various items: soil, air, water and human risks and safety as shown. ➤ Methodologies for quantifying these indicators have also been provided and will be used all along the NoAW project. ➤ Preliminary insights on European legislation and threshold limits have been provided when available. <p>These indicators will be further used in different tasks of the project to implement the sustainability of the various processes by:</p> <ul style="list-style-type: none"> ➤ Serving as base for the Life Cycle Assessment (LCA) Analysis in WP2. ➤ Be used in the stakeholder’s surveys that will be implemented in task 1.3 for investigating and mapping economic, environmental and social challenges and opportunities of agro-waste chains. ➤ Implementing the multicriteria sensitive analysis tools developed in WP2. ➤ Serving to evaluate the overall sustainability of the various wastes management processes in combination with economical and other social indicators.

3. Introduction

During the last decade the ever increasing worldwide population has been accompanied by an intensification of agriculture and growing food production, but as well by the growth of the amounts of agricultural wastes and by-products. The transformation of agricultural wastes and by-products into biofuels and value added molecules is becoming increasingly popular as a way to mitigate global warming and diversify energy sources. For this purpose, circular bio-economy based on agricultural wastes and by-products has become a major issue for sustainable development of the agricultural sector. In that sense, new strategic approaches are required and new productive concepts are gaining momentum (Monlau et al., 2015). The transition to a bio-based industry is taking place, among others, by means of:

- (1) A progressive integration (“industrial symbiosis”) of different conversion technologies, establishing functional connections and links across different processes such as extractive, biological and thermo-chemical processes.
- (2) The development of new value-chains implementing the “cascading” biomass utilization scheme, where the output of one process becomes the input of the following one (thus also targeting the “zero-waste” goal).
- (3) Processing biomasses in compliance with the “closed-loop” principle, i.e. favoring the returning of plant nutrients into the soil, thus making the farming system more ecologically sustainable and preserving soil quality, its fertility and organic matter (the latter to be also intended as an influential “carbon stock”).

The **NoAW “No Agricultural Wastes”** project will develop an advanced chemical and biotechnological platform to convert a large set of solid assets (wheat straw, winery wastes) as well as manure. The anaerobic digestion (AD) process will correspond to the benchmark of the process. Indeed, AD is a mature process well developed in Europe for the agricultural waste management (*i.e.* France has about 200 biogas plants of agricultural origin, compared with more than 8000 in Germany and 1000 in Italy; by 2025, the target is to increase to almost 1500). Nonetheless, farm biogas plants development is too dependent of the incentives of each country and are not always profitable due to limitation of heat use but also under-developed digestate management. For these purposes, a cascaded biorefinery scheme with upstream and downstream processes of the AD process will be investigated during the NoAW project. **WP3** and **WP4** are the technical core of the project dedicated to the experimental verification of existing conventional technique (AD) and innovative integrative biorefinery concept with downstream or upstream AD valorization routes. **WP3** aims at providing in-depth knowledge on both “conventional anaerobic digestion” (AD) and advanced AD connected technologies to improve the efficiency of agro-waste management. **WP4** aims to increase opportunities for agro-waste valorization in strong interconnection with AD technology by rationally enlarging the spectrum of conversion process and product portfolio. Producing multiple products will enable to step up to an agro-waste bio-refinery strategy, in a manner that seeking zero waste producing, while maximizing the value derived from the agro-waste feedstock. This objective implies to gain better knowledge and understanding of complex agro-waste conversion routes. The main objective will be to develop and validate through **WP3** and **WP4** the economical and energetic feasibility of the processes at lab-scale (TRL3-4) but also pilot-scale for the most promising valorization routes (TRL6-8).

Besides to evaluate the technical-economical performances of these innovative wastes management conversion processes, it is of prime interest to assess also the environmental and human sustainability of the various processes. The evaluation of both the environmental and human impacts require the development of appropriate indicators as previously defined by other studies (Andrew, 1998; McBride et al., 2011). For these purposes, the main objectives of deliverable **D1.1** are:

- The development of **key sustainability indicators** for assessing the environmental and human impact of the agricultural wastes management routes that have been selected.
- Determination of **methodologies** that will be used to quantify or evaluate the indicators.

4. Results

4.1. Wastes management Processes developed in the NoAW Framework

The main agricultural wastes that will be investigated during the project have been selected to represent the large range of agricultural wastes which are generally generated with a crop residue (wheat straw), animal husbandry waste (animal manures) and an agro-food waste (winery wastes).

➤ **Wheat straw (WS)**

Among different lignocellulosic raw materials, WS is very suitable for biorefinery approach (Tomás-Pejó et al., 2017). The production of 1 kg of wheat grain generate of 1.1 kg of straw (Bamaga et al., 2003) and according to the Food and Agricultural Organization (FAO), 715 million tons of wheat straw were produced in 2013 worldwide (FAOSTAT, 2016). Taking into account the wheat straw already used for animal feeding/breeding and soil maintenance, about 60% of the world production is still available for energy production purposes (varying from the geographical localization), missing clearly of valorization outputs (Kim and Dale, 2004).

➤ **Winery Wastes (WW)**

Grape wine is among the most important alcoholic beverages in the world, with a continuously rising demand, currently sizing at 25 billion liters (Zacharof, 2016). France is the first wine producing country in the world with 41.4 million of hectoliters or 16.4 % of the global production each year, followed by Italy with 40.1 million of hectoliters or 15.9 % and Spain with 30.4 million of hectoliters or 12.1 % (Zacharof, 2016). The winery sector is thus a high waste stream producer and for this reason, winery wastes have been selected as model substrate concerning agro-food wastes generated from the agricultural sector. Winery waste can be divided into two main categories, solid and liquid waste. Solid waste is generated during the collection of grapes and liquid waste is generated during the wine making process. The main winery wastes are grape stalks, grape pomace and grape seeds and wine less (Da Ros et al., 2016a; Da Ros et al., 2016b; Zacharof, 2016).

➤ **Animal Manures (AM)**

Animal manures is composed of a liquid mixture of urine, feces, water and litter material. Generally, wheat straw is one of the main wastes of the animal husbandry sector (Holm-Nielsen et al., 2009). If handled properly, manure can represent a valuable resource for its nutrients recovery for agriculture. Nonetheless, when untreated or poorly managed, animal manure can become a major source of air and water pollution by nutrient leaching, ammonia evaporation and pathogen contamination (Holm-Nielsen et al., 2009). Furthermore, in **task 4.1** of the project other kinds of agricultural wastes will be investigated such as tea, trap seed and bilberry, wastes of potato industry.

Fig. 1 describes the main principles of the waste management processes that will be developed in the NoAW framework. In brief, the Anaerobic Digestion (AD) will represent the benchmark of the project in task 3.1 with a classical route where biogas and digestate for soil application are produced. Then several innovative valorization routes integrating upstream or downstream processes on the AD process will be investigated. All these processes are developed more in depth in the following paragraphs.

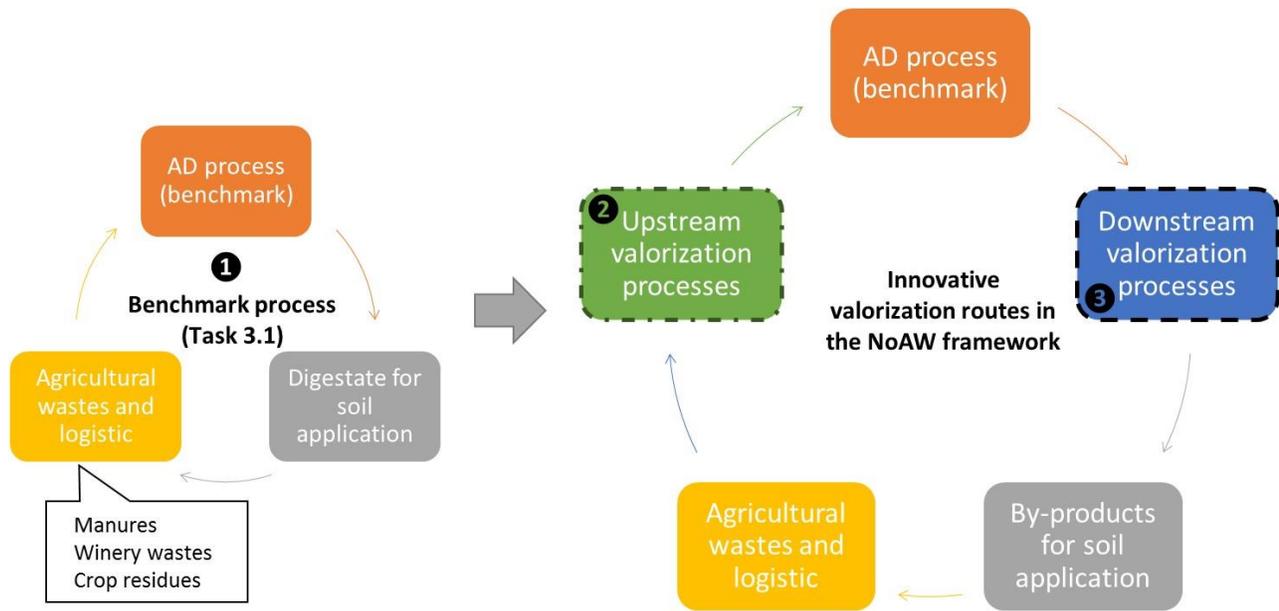


Fig. 1. General schemes of the agricultural wastes management scenarios investigated under the NoAW framework compare to the Anaerobic Digestion (AD) benchmark.

Below, a brief description of the main wastes management conversion processes investigated under the NoAW project through **WP3** and **WP4** are provided:

1 Anaerobic digestion (benchmark process)

Anaerobic digestion (AD) is a biological process by which organic matter is transformed in absence of oxygen into biogas (a mixture of carbon dioxide and methane), during four steps (hydrolysis, acidogenesis, acetogenesis and methanogenesis) will be investigated as the benchmark for the agricultural wastes valorization (**Task 3.1, Schiessl**). AD process has been found to be a promising route for the valorization of agricultural wastes such as manure, crop residues and winery wastes (Da Ros et al., 2016b; Monlau et al., 2013). The biogas produced can be valorized as transport biofuel or injected in the national gas grid (biomethane after a purification step) or further converted into heat and electricity through a Cogeneration (Combined Heat and Power - CHP) system. The last point is consistent with the present development of agricultural anaerobic digesters in European countries where biogas, in most of the cases, is converted by CHP. Electricity can be sold to the public grid at a fixed rate and provide economic benefits to farmers. The price of the electricity is dependent of the National policy and varies between the European countries (Monlau et al., 2012; Sambusiti et al., 2013). Nonetheless, the recalcitrant structure of some agricultural wastes such as wheat straw mainly composed of lignocellulosic fibers can limit their biological conversion through AD process and pretreatments should be carried out (Ariunbaatar et al., 2014; Carrere et al., 2016; Monlau et al., 2013; Zheng et al., 2014). **Task 3.4** will study pre-treatments (physicochemical and enzymatic) of recalcitrant fractions of agricultural waste/by-products (straw and manure fibers), in order to improve the performance of conventional AD and further valorize the resulting pre-treated effluent of the anaerobic digestate through additional conversion. Digestate corresponding to the anaerobically non-degraded fraction is mainly composed of recalcitrant fibers (cellulose, lignin) and rich in nutrients. For this purpose, so far, digestate has been mostly used at farm-scale for improving soils or as fertilizer (Monlau et al.,

2015b; Sheets et al., 2015). To date, digestate is generally mechanically separated (belt press, sieve drum, screw press, sieve centrifuge, rotary screen and decanter centrifuge) into liquid and solid fractions that are stored separately for easy handling and transport (Monlau et al., 2015b). Under the NoAW project, the optimization of the use of anaerobic digestate from a full scale plant will be investigated regarding the agronomic properties and performing field's trials (**Task 3.1**).

② Two stages anaerobic digestion for hythane and carboxylates production

The “conventional” AD process could be turned into two-stages processes where the first step of hydrolysis and acidogenesis are separated from the methanogenesis step. In that case, two products of interest could be produced in the first stages called “dark fermentation” as carboxylates and hydrogen (Arslan et al., 2016; Monlau et al., 2015a). The two-stage H₂/CH₄ process will be investigated through the **task 3.2 (INNOVEN, INRA-LBE)**. The two-stage H₂/CH₄ process presents several advantages compared to the conventional one stage CH₄ process since it leads to the selection and enrichment of specific and different microbial consortia in each stage, resulting in a better overall process stability (Liu et al., 2013; Reginatto and Antônio, 2015). In the first stage, low pH and short hydraulic retention times, (HRTs) are maintained in order to favor the fermentation of lignocellulosic residues into hydrogen and volatile fatty acids (VFAs) by enhancing the growth of H₂-producing bacteria. These bacteria are less sensitive to substrate fluctuations than methanogens. In the second stage, neutral pH and longer HRTs are maintained to develop the growth of acetogens and methanogens for further conversion of VFAs to methane and carbon dioxide (Monlau et al., 2015a). Another potential advantage of turning the AD process into a DF-AD is the possibility to produce hythane. Hythane is a mixture of hydrogen (10–25%) and methane (75–90%). Hythane has advantages over methane including for a wider range of flammability, faster flame speed, shorter quenching distance and lower carbon dioxide emission. Similarly, hythane can be used as transport fuels or in CHP systems to produce electricity and heat (Liu et al., 2013).

③ Integration of value added molecules/products generation upstream of the AD biorefinery process (task 4.1)

Agro-waste presents potentially high opportunities as a source of added value bio-molecules and bio-products. However, its molecular complexity and heterogeneity make difficult its eco-efficient conversion. Presently, only 5% of chemicals are bio-based, whereas it is known that agricultural products, lignocellulosic material and waste biomass could be converted to platform chemicals (Pfaltzgraff et al. 2013) and then to secondary chemicals, intermediates and final products (Jang et al. 2012). Therefore, NoAW activities in WP4 (task 4.1) aim at improving the efficiency of the agro-waste exploitation.

A range of innovative eco-efficient conversion routes of waste, upstream of the AD process, to high-value molecules and materials will be investigated.

Production of bio-chemicals – As well as developing knowledge about composition, molecular structures and characteristics of agro-waste, advanced selective extraction processes will be applied to extract bioactive molecules. Supercritical fluid extraction and single or mixed cell wall digestion enzymes (pectinase, xylanase and cellulase), in combination or not with organic solvents, will be adapted to winery wastes (pomaces) (RISE, UNIBO) to extract bio-molecules (such as polyphenols and phenolic acids) with functional properties (antioxidant, antimicrobial and anti-tyrosinase). Tannins (proanthocyanidins) will be extracted from wine shoots and stalks by grinding (INRA). Shear emulsifying assisted enzymatic hydrolysis will be developed to extract fiber and starch from potato starch processing waste and ultrafiltration used to obtain proteins from wastewater. Dietary fibre, potato protein, and nutritional and health-related food products will be the main products (IAPPST).

Building blocks and polymer development – Bio-molecules extracted from agro-waste can be valorized by the development of innovative and eco-efficient cascading conversion processes to produce new bio-polymers. Aromatic molecules, such as phenolic acids (for example, vanillic acid), if characterized by high purity, could be exploited as building blocks for polycondensation reactions to synthesize new (co)polyester structures, which match properties of the petro-derived PET (UNIBO). In this way, according to the trends of the academic and industrial interests (Mialon et al, 2010; Gandini et al., 2009; Gioia et al., 2016), it will be possible to propose new sustainable synthetic routes of an alternative polymer to PET, that covers the 7% of the European plastic demand and is exploited mainly for packaging applications (Plastics-the Facts 2016, PlasticsEurope). Polyphenol mixture, with significant antioxidant properties, will be used as additive to formulate bio-polymers and obtain new fully bio-based materials with high performances (ITRI, UNIBO).

Based on the extension of 2 recently patented processes, tannins (proanthocyanidins) obtained from vine shoots and stalks will be converted into multifunctional phenolic building blocks to synthesize technical speciality chemicals, emulsifiers, and, by grafting aliphatic charged chains and further functionalized, new polymers (polycarbonates). The substitution of BPA by biosourced polyphenols will offer a large innovative opportunity for applications of the new materials in the packaging sector and the large structural diversity of natural polyphenols will be exploited in specific applications not available for monostructural chemicals, such as BPA (INRA, UM).

Bio-composites – Based on knowledge and know-how acquired on the development of PHBV/wheat straw fibres biocomposites in the frame of the European EcoBioCAP project (Berthet et al., 2015, Berthet et al., 2016, Berthet et al. 2017), wine shoots will be exploited in the NoAW project to produce lignocellulosic fillers by combining dry grinding, sorting (electrostatic separation and air classification). One recurrent drawback of natural fillers is their poor compatibility with polymer matrices owing to the intrinsic hydrophobicity of most polymers that contrasts with the hydrophilicity of lignocellulosic fillers. To overcome this problem, the surface of lignocellulosic fillers will be functionalized using solvent-free hydrophobisation technologies (plasma or gas-phase esterification) (UM). Biocomposites will be produced using polymers prepared in Tasks 3.3, 4.1, 4.3 (UM, UNIBO). Performances in usage conditions (food contact migration) and impact on soil quality (biodegradability, fertility) will be studied (UM).

Succinic acid from carbohydrates-rich agro wastes – Succinic acid is one of the top commodities and could replace many petro-based chemicals (Lin et al., 2014b). However, there is a lack of studies on the use of mixed agro-waste for the succinic acid fermentation and on engineered strains able to metabolize carbohydrate-rich agro waste. Therefore, production of succinic acid from carbohydrate-rich agro-wastes will be developed based on an engineered *Y. lipolytica* strain already improved for succinic acid production, available from SEE. The performance of the fermentation process, in terms of yield, productivity and by-product reduction (such as acetic acid), will be optimized: (1) at the strain level by metabolic and revolutionary engineering to adapt it to the potential substrates and inhibitors specifically present in wastes; (2) at the process level by optimizing nutrient supplementation, environmental cultivation conditions and the design and implementation of various bioreactor operating strategies (SEE, INRA).

4 Integration of value added molecules/products generation downstream of the AD biorefinery process: VFA valorization

Innovative eco-efficient conversion routes of VFA, obtained from the 2-step AD process, toward high-value molecules and materials will be investigated (task 3.3 and 4.3).

PHAs production (Polyhydroxylalkanoates) – PHAs are linear polyesters produced in nature by bacterial fermentation of sugars or lipids; they are fully biodegradable, characterized by a broad range of

compositions available and, then, by different properties that can be tailored according to the incorporation of different monomers into the main structure (Laico et al., 2013). Nowadays, PHAs are attracting much attention as alternative and fully sustainable polymeric materials. The VFAs produced in the first stage of the two steps AD process (liquid digestate) will be used for the PHAs production through biological pathway using mixed cultures (task 3.3) (UNIROMA).

Moreover, PHA will be produced from VFAs using light as the sole energy source (IBET). In this way PHA production would require less energy consumption (Frandinho et al., 2014). Key operational parameters affecting photofermentation will be addressed, including the impact of different VFA profiles on the polymer composition and yield (task 4.3).

The PHAs will be further used in an extrusion/compounding process for the production of bioplastic.

Concentrated and functionalized VFAs: building blocks for polymers (task 4.3) – VFAs residues streams are too diluted aqueous effluents and mono-functional molecules. Concentration of VFAs-rich effluents will be increased by membrane-based technologies, i.e. nanofiltration. The addition of hydroxylic and carboxylic functionalities to VFAs will be investigated at the cathode of bioelectrochemical systems based on monooxygenase enzymes and hydrocarbons oxidizing microbes. Functionalized short chain fatty acids (i.e., hydroxylated FA, dicarboxylic acids, etc.) will be obtained and exploited as monomers for polycondensation reactions to prepare bio-based polyesters (UNIBO).

5 Integration of AD process in a biorefinery concept through downstream innovative valorization routes for the solid anaerobic digestate:

At farm scale, for a better handling and valorization, digestates are generally separated in a liquid and solid fraction (i.e. previously described in the section anaerobic digestion). Recently, Santi et al., (2015) have demonstrated that the digestate produced by commercial agricultural wastes biogas plants contains a notable quantity of cell wall polymers (i.e. mainly fibers). These residues could potentially be used in biorefinery processes. For this purpose, several alternative routes beyond land application could be considered for the solid digestate valorization (Monlau et al., 2015b; Sheets et al., 2015). Among them, pretreatment followed by bioethanol fermentation but also thermo-chemical process (i.e. pyrolysis) will be investigated under the NoAW project.

The **bioethanol** fermentation on solid digestate will be investigated in the **task 3.4** (AAU) and **4.2** (INRA) in presence or not of pretreatment (i.e. reactive extrusion). The bioethanol fermentation is commonly composed of two steps: enzymatic hydrolysis and fermentation that can be realized separately or simultaneously. According the scheme used, two processes are distinguished: enzymatic hydrolysis is performed separately from fermentation, as separate hydrolysis and fermentation (SHF), or simultaneously, as simultaneous saccharification and fermentation (SSF). More recently, Direct Microbial Conversion (DMC) have been proposed as the logical endpoint in the evolution of bioethanol from lignocellulosic matrix (Balat, 2011). DMC combines enzyme production, enzymatic hydrolysis and fermentation (Balat, 2011). After the bioethanol fermentation step, a distillation process is required for separation and purification of ethanol from water (Limayem and Ricke, 2012). Concerning the microorganisms used for bioethanol production, traditionally facultative anaerobic yeast *Saccharomyces Cerevisiae* sp. and the ethanologenic *Zymomonas Mobilis* sp. are the most often used for bioethanol fermentation as they provided interesting ethanol yield (Limayem and Ricke, 2012). Nonetheless, such microorganisms are unable to ferment xylose monomers (Balat, 2011; Sarkar et al., 2012). For this purpose, actual development and optimization to render cost effective new strains that are able to convert both C₅ and C₆ sugars are under research (Balat, 2011). Among these strains, we can mention the yeast *Pichia Stipilis* and the bacteria *Escherichia Coli* (Limayem and Ricke, 2012). Due to the recalcitrant structure of the lignocellulosic fibers of anaerobic digestate, a post-treatment step could be recommended to improve the bioethanol rate conversion.

Pyrolysis is another promising process for the solid digestate valorization that will be investigated during the **task 4.2** of the project (INRA). Pyrolysis is a thermo-chemical process that converts organic matter in absence of oxygen into three phases: pyrolysis gas, bio-oil and bio-char (Manara and Zabaniotou, 2012; Samolada and Zabaniotou, 2014). Due to its high calorific content, pyrolysis gas can represent an interesting supplementary energy source that can be further converted into heat and electricity using internal combustion engines. The bio-oil produced is of primary interest as it can replace diesel in internal combustion engine to produce electricity (Manara and Zabaniotou, 2012). Literature studies proved that, through the pyrolysis process, renewable energy (from gas and bio-oil) as well as valuable solid materials (biochar) can be produced; the latter is proposed as carbon sequestration agent by land application but also as soil amenders (Kookana et al., 2011; Laird et al., 2010). Biochar produced from pyrolysis process due to his rich phosphorous content could represent also a good fertilizers candidate on condition to improve the biodisponibility of the phosphorous. Alternatively, biochar, due to its high porous reactive surface and structural characteristics, may also be used for environmental depollution applications including the removal of large toxic molecules (Inyang et al., 2012) and the reduction of nutrients leaching (*i.e.* nitrate, ammonium, phosphate) in soil (Yao et al., 2012).

Composting is another interesting solution for the management of solid digestate into compost to a state in which it can be handled, stored, and applied to the land without adversely affecting the environment. Composting is the biological degradation process of organic matter (like solid digestate) under controlled aerobic conditions, with the production of a biologically stabilized material (*i.e.* compost), which is not oxygen consuming, nor able to generate phytotoxic metabolites (Cesaro et al., 2015). Composting can be realized at different scales (*i.e.* domestic, industrial). At industrial scales; different ways generally linked to the feedstocks can be applied: open windrow composting, composting in clamps/compartments with forced aeration and composting in close reactors (ADEME, 2012). The fermentation phase is characterized by the degradation of organic matter by thermophilic species. It is followed by a maturing phase with degradation of cellulolytic and ligno-cellulosic compounds and humification reactions (Wery, 2014). The decomposition process could be aided by shredding the plant matter, adding water and ensuring proper aeration by regularly turning the mixture. The selection of the bulking agent in combination with the solid digestate is crucial in order to optimize the composting performances and to improve the quality of the final compost. (Bustamante et al., 2013) have investigated the composting performances in presence of various bulking agent such as wheat straw, exhausted grape marcs, vine shoot pruning and pepper plant pruning. The main factors in the control of composting include: (i) environmental parameters (temperature, moisture content, pH, aeration) and (ii) substrate nature parameters (C/N ratio, particle size and nutrient content) (Bustamante et al., 2012; Bustamante et al., 2008; Miyatake and Iwabuchi, 2006; Saludes et al., 2008). A good compost stability is achieved when the dynamic respiration achieved a value lower than $1000 \text{ mgO}_2 \text{ kg VS}^{-1} \text{ h}^{-1}$ (Adani et al., 2006). The EU considers the solid fraction of digestate as a waste (EEC, 2008), so that it cannot be freely marketed and used, if not composted. The final product of composting can be defined as a stabilized material that can be used as an amendment in agricultural soils (Bustamante et al., 2012; Bustamante et al., 2008). The composting of the solid digestate is a promising technology for improving its quality reducing the odor emission by VFAs reduction, reducing the moisture content, and also the potential phytotoxicity towards plants (Bustamante et al., 2012; Bustamante et al., 2013). In the **Task 3.1**, an optional composting step on the solid fraction of the digestates will be investigated, along with the agronomic properties of the digestate produce.

4.2. Boundaries of the studies for selection of sustainability indicators

The boundaries for which we have to define key indicators that can affect positively or negatively the environmental assessment during agricultural wastes management are described in **Fig.2**. These boundaries will be further discussed during the project with the Environmentalist partner and KESP and could be modified/expanded during the project. As previously mentioned in the **section 4.1**, the main

agricultural wastes that will be addressed through the NoAW project are straw, manure and winery wastes.

Then, each wastes management process investigated on the NoAW framework are divided in four main functional units:

- **Function 1:** Feedstock handling and pretreatment;
- **Function 2:** Wastes conversion and main end-products;
- **Function 3:** By-products as input for another application in a cascaded biorefinery scheme;
- **Function 4:** Wastes generation.

It is important to notice that normally in the concept of the NoAW partner, **the function 4** will be limited as the “cascading” biomass utilization scheme will be implemented, where the output of one process becomes the input of the following one (thus targeting the “zero-waste” goal).

Note 1: From these system boundaries, all the cropping steps (i.e. tillage, dressing sowing, etc.) are not considered as already included in the conventional agricultural system. In these boundaries, are included all steps that could have an impact due to the new management waste system developed.

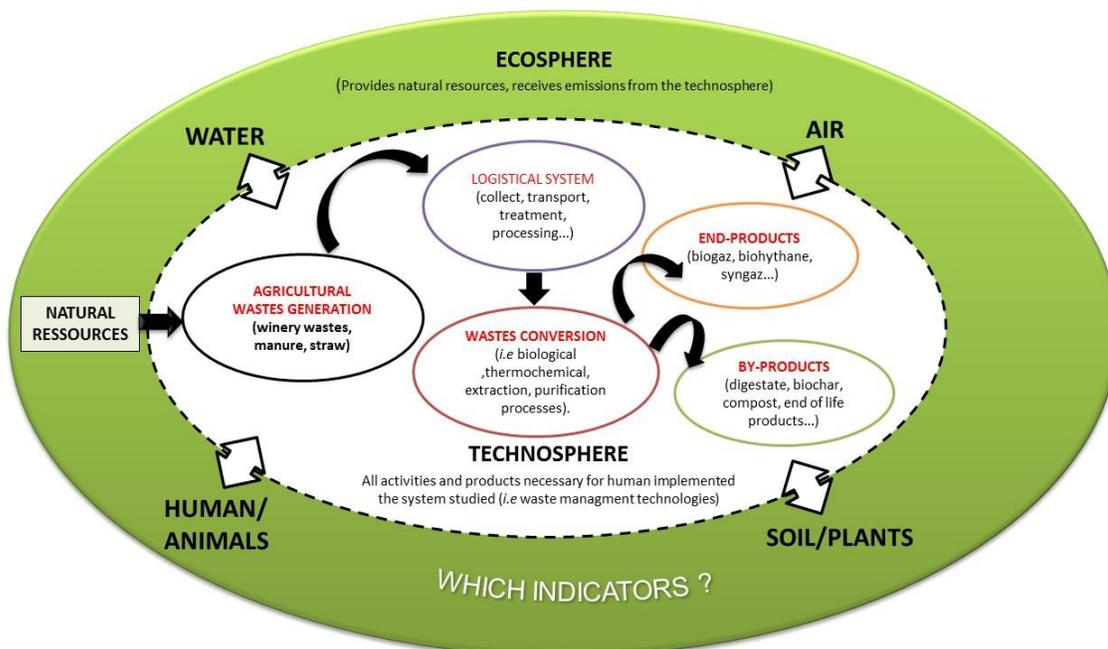


Fig.2. Impact of the waste management technologies routes on the ecosphere: Which selection of key indicators to assess the environmental impact?

For each processes (of the NoAW project, **Table 1**), we should define key indicators permitting to compare to “without” situation (without application of the process, that means to use the classical valorization route) and the “with” situation (with application of the process developed under the NoAW project). The main objective being to determine key **environmental sustainability** indicators for assessing the impact of the innovative wastes management conversion routes on the various items of the ecosphere (i.e. air, water, soil). Besides, environmental sustainability indicators, human sustainability indicators will

also be assessed (description in **part 6**). To determine these key indicators, several criteria have been applied (some of them taken from previous works McBride et al., 2011; Efrogmson et al., 2014):

- The selection of the **key indicators** has been made by partners involved in task 1.5 after discussions with specific partners involved in WP2, WP3 and WP4. The sharing of indicators between the various partners involved in **task 1.5** is described in **Fig.3**.
- **Independent.** Indicators have to be independent from the feedstock and be relevant for any biomass.
- **Quantifiable.** For environmental sustainability indicators to be quantifiable according methodologies available within the NoAW consortium partners.
- **Practical.** Indicators should be straightforward and inexpensive to measure or simulate.
- **Predictable** in response. Be able to reflect the impact of the various functions of the wastes management routes on the item of the ecosphere (*i.e.* water, air, soil, etc.).
- **Anticipating.** Indicators should be relevant for conventional wastes management processes (under industrialization) but also for innovative technologies still under lab-scale development.
- **Sufficient and non-redundant** when considered collectively. Indicators should not be strongly correlated but sufficient to assess the diversity of the processes.
- **For human indicators**, it is required to assess the risks and safety of the current technologies but also from the innovative scheme of valorization routes still under lab scale development.

Finally, for each environmental sustainability indicator, each partner will propose methodologies to quantify these indicators during the development of the processes in **WP3** and **WP4**.

Note 2: It is important to clarify that the list of indicators developed below is an exhaustive and relatively large list integrating the diversity of the wastes management processes that will be developed through the NoAW project.

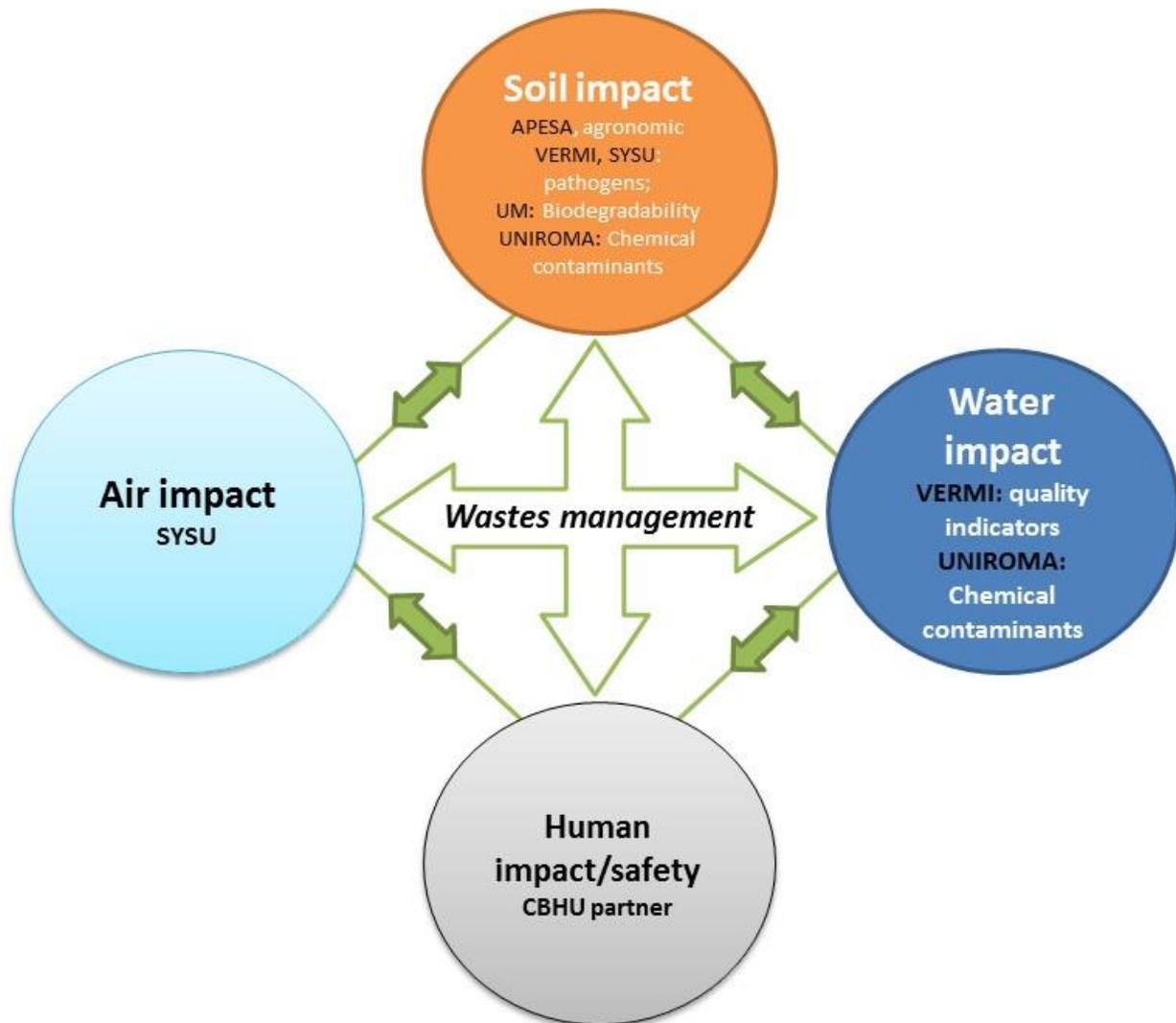


Fig. 3. Work distribution on the task 1.5 for the various partners involved.

4.3 Environmental Sustainability Indicators

Sustainability Indicators to assess the impact of the innovative wastes management conversion processes on the ecosystem over time are needed to determine the best suitable biorefinery scheme under which wastes uses are sustainable. In the 1.5, the first work consists in determining key indicators to assess the **environmental sustainability** of the wastes management routes (Fig. 4). A series of key indicators on the three main environmental systems “soil, water, air” was assessed. Then, suitable methodologies along with their references have been established.

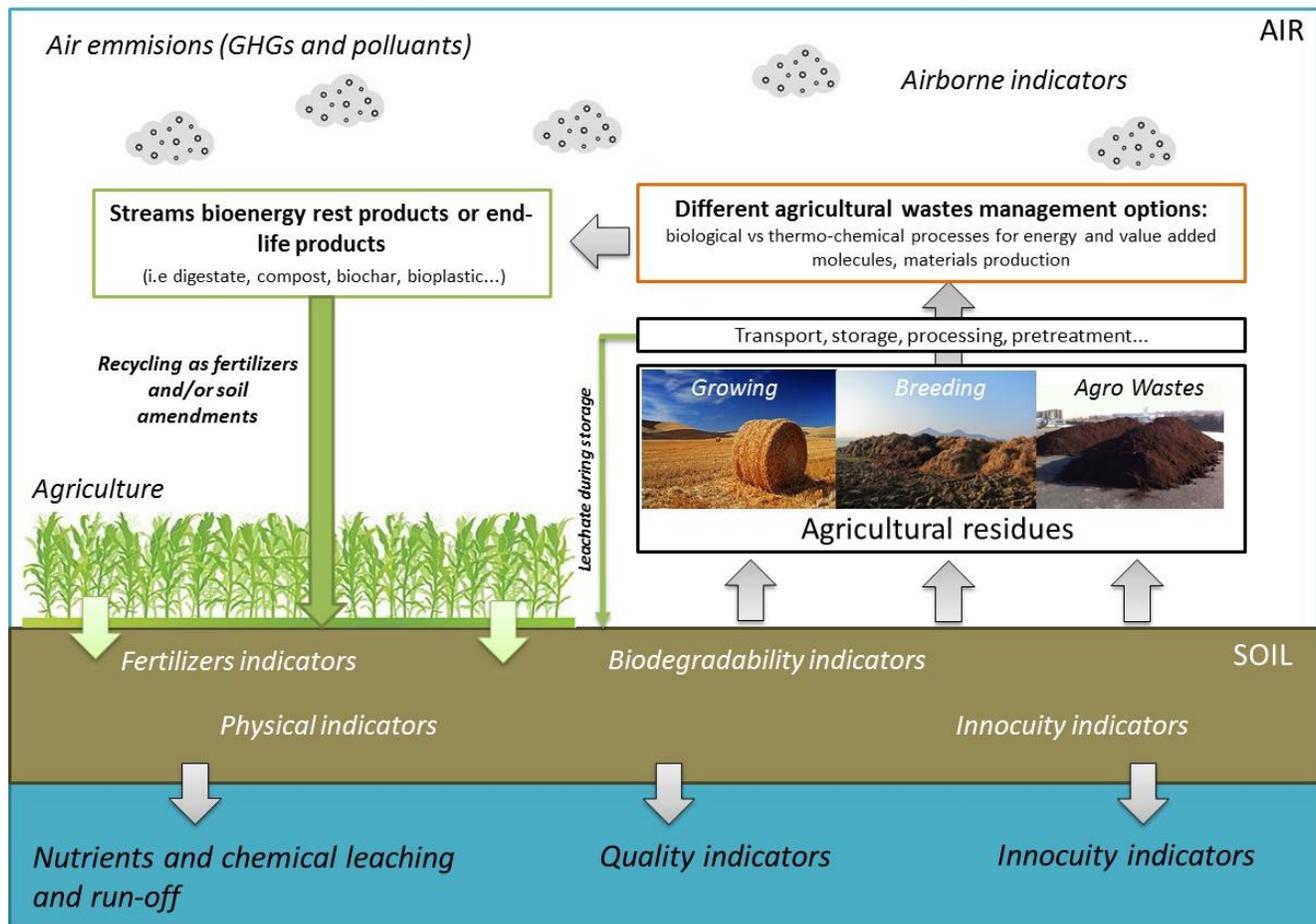


Fig. 4. Overall scheme of the potential environmental impact that wastes management processes developed through the NoAW framework could exert on the various items of the ecosphere: soil, water, air.

4.3.1 Soil indicators

Soil indicators are important to monitor as the wastes management processes developed through the Project can affect directly the soil. For this purpose, emissions that could have an impact (positively or negatively) on the soil quality, soil organisms, soil productivity and plant growth have been assessed. The soil emissions during wastes management conversion can occur mainly:

- Leaks during storage of agricultural wastes or streams of waste management processes.
- Release of leachate during the wastes handling or during processing.
- Return to the soil of by-products (*i.e.* digestate, compost, biochar, bioplastics, etc.).

Furthermore, soil indicators are of prime importance as the soil item is directly in interaction with air and water. The soil indicators are divided in two main classes as efficiency indicators (fertilizers, amending, physical-chemical properties, etc.) and innocuity parameters (inerts and contaminants). Indeed, land application of by-products may introduce into the soils physical, chemical and biological contaminants which may jeopardize their long term agricultural productivity (Nkoa, 2014).

4.3.1.1 Efficiency indicators

Table 1. Efficiency indicators recommended to assess for environmental sustainability loads of the wastes management processes developed on the soil item.

Indicators Family	Indicators names	Description	Units or Parameters quantified
Fertilizing values	Nutrients load (linked to the by-products amount)	Nutrients load (N, P) applied per ha	kg N, P / ha
	N, P, K, S	Nutrients content of the by-products (<i>i.e</i> digestate, compost, biochar, etc.)	kg nutrients / tons or m ³
	Water-extractable P	Fraction of P available for plant	kg P / P tot
	N mineralization	Fraction of N which is mineralized and thus available for plants	kg _{eq. N} / N tot
Amenders values	Organic matter	Determination of the organic matter	kg organic matter / t TS
	C/N	Determination of C and N content	kg N, C / t TS
	C mineralization in soil	Determination of the C which is mineralized on a one year	kg CO ₂ / C org tot
	Biodegradability in compost	Determination of biodegradation in aerobic conditions of bioplastics	% relative biodegradation (vs cellulose)
Physical-chemical properties	pH	Determination of the pH (H ₂ O)	no unit
	Water Holding Capacity (WHC)	Determination of the WHC of soil and by-products	kg water / kg dry soil or by-products
	Capacity of Exchange Cations (CEC)	Determination of the CEC of soil and by-products	cmol (+) kg ⁻¹
	Bulk density	Determination of the bulk density of soil and by-products	g cm ⁻³

• Fertilizers properties

Fertilizers are applied to soil to promote plant nutrition thanks to the provision of macronutrients and micronutrients (Teglia et al., 2011). The fertilizers potential of exogenous organic matter (*i.e.* compost, biochar, digestate) is thus an important indicator to be addressed when such biomasses are used as fertilizers. The fertilizers value is based on the nutrients content and especially the three main nutrients (N, P, K). Other nutrients such as S, Mg, Ca can also be monitored. However, the fertilizers potential of an organic product is not only estimated by the total amount of the three main nutrients (N, P, K) but also by their availability to plant nutrition. Such nutrients availability can be assessed as water soluble concentrations (for P elements) but also through nutrients mineralization during soil incubation (for N elements) (Teglia et al., 2011).

Nitrogen (N) from organic matter comes in both organic and inorganic forms. Inorganic N, mostly ammonium (NH₄⁺) and nitrate (NO₃⁻), is readily available to plants. However, organic N before to be taken up by plants must first be converted to inorganic forms. This process, which is completed by soil microbes is called mineralization. The mineralization of N could be assessed by short term incubation in

soil (Albuquerque, 2012; Hartz; et al., 2000). Phosphorus is another essential macronutrient for plants and is generally supplied to soil in the form of phosphate fertilizers. In order to meet plant P requirements, approximately 15 million tons of P fertilizer is globally applied to agricultural land each year (Wang et al., 2012). However, only 5–30% of P applied is taken up by the crop in the year following application (Price, 2006). A substantial amount of the applied ortho-phosphate is often lost to the aqueous environment via run-off (Kuligowski et al., 2010).

The nutrients loads (kg / ha) applied to the soil culture is another essential parameter to be monitored to avoid deficit but also excess of nutrients that can have a detrimental impact on environment. The nutrients load of exogenous organic matter (EOM) to apply to the fields will depend on a set of various parameters among them:

- Crop to be grown, previous crop grown and expected crop yield;
- Soil type and existing reserves of nutrients in the soil (carried out by periodic soil sampling, agrochemical analysis and mapping of soils);
- Recommended nutrient requirements for the plant culture, generally between 80-275 kg N ha⁻¹ (Gell et al., 2011). Nonetheless, in livestock intensive and restrictive area, the European Nitrate Directive has set a threshold level of 170kg nitrogen per hectare per year for manure spreading, with specific spreading date restrictions when crops are not in need for nutrients (autumn/winter) (Council Directive 91/676/EEC, 1991);
- The period and method of application and incorporation of the EOM in the field;
- Expected utilization percentage of nitrogen in EOM and addition or not of industrial mineral fertilizers (as it is quite complicated to obtain the suitable N and P requirement of the culture need only by EOM addition).

It is of prime importance to adapt the nutrients requirement to these different indications to avoid an excess nutrients supply that can cause environmental and human damages. Water quality can be damaged by excess of P and Nitrate leading to eutrophication. An excess of nutrients could also impact the air quality by excessive emissions of NH₃ which have an impact on human health and on the environment, as they contribute to the acidification process in soil, eutrophication of waters and ground-level ozone pollution, together with other pollutants. More details about this aspect will be provided in the specific section for the air and water sustainability indicators.

The various exogenous organic matter are a source of fertilizers potential that will depend on the feedstock used but essentially on the processes applied. The balance between organic and mineral forms of carbon and nitrogen is essential to state on the agronomic use of an exogenous organic matter (Teglia et al., 2011). In general, products rich in mineralizable carbon and soluble mineral nitrogen will rather be used as fertilizers than soil amenders. For this purpose, liquid digestate are preferentially used as fertilizers whereas solid digestate, compost and biochar have a greater potential as soil amendment.

At farm scale, digestate is generally mechanically separated into liquid and solid fractions that are stored and handled separately. The liquid fraction is rich in nitrogen (N) and potassium (K), whereas the solid fraction retains great amount of phosphorus (P), ash and organic matter (mainly recalcitrant fibers) (Liedl et al., 2006). Liedl et al. (2006) have investigated the fertilizer potential of liquid and solid effluent from thermophilic anaerobic digestion of poultry waste. Interestingly, application of the solids as a field crop fertilizer for vegetables and blueberries resulted in lower yields than the other fertilizer treatments, but in an increase in soil phosphorus over a four-year period. Application of the liquid digestate on grass and vegetable plots resulted in similar or superior yields to plots treated with commercially available nitrogen fertilizers.

In biochar, most of N and S compounds volatilize above 200 and 375°C whereas K and P volatilize between 700 and 800°C and thus these two elements are generally conserved in biochar produced from

pyrolysis process (Kookana et al., 2011). Biochar from pyrolysis process have been identified as an interesting alternative to concentrate the P content from the initial feedstock in a reduced carbonaceous fraction. Nonetheless, it has been also demonstrated that the P plant availability from biochar can be low requiring the addition of mineral fertilizers (Kuligowski et al., 2010). Biochar from pyrolysis process can be used as phosphate fertilizer to maintain a P level in the soil in the time, but not as a starter fertilizer due to its low P availability (Kuligowski et al., 2010; (Zhang et al., 2016). In parallel, biochar in combination with mineral fertilizers and/or liquid digestate will favor the nutrients exchange and their retention in the soil due to their physico-chemical properties and their nutrients and water retention capacity (Xu et al., 2012; Zhang et al., 2016).

In other organic matter than liquid digestate (*i.e.* solid digestate, compost, biochar), besides the nutrient content (N, P, K, etc.) it is more the plant availability of the nutrients over time that will define their fertilizers properties. Below, techniques used to assess the N and P availability of such organic matter will be described. Water-extractable P is generally assessed to determine the readily plant-available P and is a good indicator of possible nutrients run-off and leaching. To assess the N availability of exogenous organic matter, N- mineralization soil test are generally applied (Hartz; et al., 2000). Mineralization test of nitrogen allows the quantification of mineralized nitrogen and nitrogen availability for plants. Generally N mineralization decreases according the following order: Digestate>Compost>Biochar (Hartz; et al., 2000; Teglia et al., 2010). N mineralization can be influenced by the C/N ratio. Organic nitrogen is predominantly converted into inorganic forms that are either used in new microbial synthesis or released into the soil once the product is applied on land. If there are both a low concentration of organic carbon and a larger quantity of nitrogen in respect to the requirements of microorganisms, nitrogen will be mineralized and released in soil. On the contrary, if nitrogen quantity is smaller than microbial requirements, inorganic nitrogen contained in soil will be used to complete the biodegradation process leading to nitrogen immobilization. Thus C/N of organic residues must be well balanced in order to assure their stability once applied on soil (Teglia et al., 2011). Given the high C/N ratios generally observed for biochar, a N immobilization can be expected, inducing plant N deficiency, which is generally not the case due to the recalcitrant nature of carbon in biochar (Atkinson et al., 2010).

As for **bioplastics**, few data are available in literature, however Adhikari et al. (2016) have shown that the degradation of bioplastics (such as poly (hydroxylalkanoate) (PHA), poly (lactic acid) (PLA), poly (butylene succinate) (PBS) and PBS-co-adipate (PBSA) in soils did not affect the nitrogen circulation.

Methodologies:

To assess the nutrients composition (N, P, K, S, Ca, Mg) protocols defined in the French standard Norm **NF U – 42-001** will be used. Water P available will be determined according to the protocol below. Briefly, each exogenous organic matter (EOM) are subjected to extraction with deionized (DI) water. A suspension of 0.1 g EOM and 30 mL of solvent are shaken in a shaker at 120 rpm for 48 h in 50 mL centrifuge tubes. The suspension is then centrifuged (4000 rpm, 15 min) and the resulting supernatant filtered through a Whatman No. 42 filter paper. The filtrate is analyzed for the amount of P extracted according to the colorimetric molybdenum-blue method. To assess the N mineralization of nitrogen, a modified protocol from the French Norm **XP U44-163** is used. Briefly, the agricultural soils is dried at room temperature and then sieved to 4 millimeters and stored in a cold room at 4 °C. A digestate load of 170 kg of nitrogen / ha is chosen. Three replicates of each of the assays are analyzed at 7 time intervals (day 0, 7, 14, 28, 49, 70 and 91). Samples are stored in a thermostatic oven at 28 ° C, moisture content will be adjusted and samples aerated on days 1, 3, 7, 14 and every 14 resting days. Finally, analysis of ammonium and nitrates are carried out by dissolving the soils in

a KCL solution, and then by determining the concentration using micro-assay kits (WTW, photolab S6).

AFNOR: XPU 44-163 Organic soil improvers and growing media-Determination of potentially mineralisable carbon and nitrogen-Method of incubation under controlled conditions (2009).

NF U42-001Engrais : Dénominations and Specifications. Partie 1 Engrais minéraux (2011).

European legislation

Different **European standards** exist with respect to **N, P, K** requirements for organic fertilizers:

- In French standards, total N, K₂O and P₂O₅ must be greater than 3 % in fresh weight and the sum of the three compounds higher than 20%, respectively for an organic fertilizer (AFNOR: FD CR 13456 2001; NF U42-001).
- German standards, on the other hand, specify that nutrient contents on a dry matter basis must be greater than 0.5 % (N), 0.3 % (P) and 0.5 % (K₂O) (Siebert 2008).
- In the current Spanish legislation for fertilizers (PRE/630/2011 2011), anaerobic digestates can-not be considered balanced fertilizer products, and they must be complemented with mineral fertilizers.
- The British standards (BSI. PAS 110 2010) do not specify any nutrient limit for anaerobic digestates, although a number of parameters such as dry matter, organic matter, pH, salt content, total ni-trogen, P, K, Ca, Mg, S, NO₃⁻, NH₄⁺, micronutrients, Cl and Na should be declared.

As concerns **for biochar**; both the IBI and EBC recommend to monitor the Total N. Furthermore, total P, K, Mg and Ca are required by the EBC whereas there are optional for the IBI. Nonetheless, no specific recommendations and threshold levels are defined.

AFNOR: FD CR 13456 (2001) Amendements du sol et supports de culture—Etiquetage, specifications et listes de produits.

BSI. PAS 110 (2010) Specification for whole digestate, separated liquor and separated fibre derived from the anaerobic digestion of sourcesegregated biodegradable materials. British Standards Institution, London, 2013.

EBC (2012) 'European Biochar Certificate - Guidelines for a Sustainable Production of Biochar.' European Biochar Foundation (EBC), Arbaz, Switzerland. <http://www.europeanbiochar.org/en/download>. Version 6.2E of 04th February 2016

IBI Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in SoilInternational Biochar Initiative - May 2012.

PRE/630/2011 (2011) Orden de 23 de marzo, por la que se modifican los anexos I, II, III, IV, V, y VI del Real Decreto 824/2005, de 8 de junio, sobre productos fertilizantes. BOE 2011 72:31871–31910

NF U42-001Engrais : Dénominations and Specifications. Partie 1 Engrais minéraux (2011).

Siebert S (2008) Quality requirements and quality assurance of digestion residuals in Germany. In: ECN/ORBIT workshop The Future of Anaerobic Digestion of Organic Waste in Europe. Nuremberg, Germany.

• Amending properties

The decline of soil organic soil matter, due to intensive cropping systems, is one of the major threats towards soil. This has encouraged the European Commission to develop a strategy for Soil conservation (Commission of the European Communities, 2006). To restore soil properties, exogenous organic matter (*i.e.* biochar, digestate, compost) could be added both contributing to the environmental issues of improving C sinks to mitigate CO₂ emissions and to the restoration of soil properties through their amending properties. A soil amendment is any material which, upon addition to the soil, would improve or maintain its physical, chemical or biological properties (Nkoa et al., 2013). Soil improvers must contain a significant part of non-synthetic organic matter in order to ensure enrichment of agricultural lands and thus improve soil quality (Teglia et al., 2011). Moreover, the distribution of poorly stabilized materials

does not fit with the optimization of carbon storage in soils due to their generally high mineralizable carbon pool and the associated high carbon dioxide (CO₂) emissions (Grigatti et al., 2014).

Several indicators can be assessed to define the amendment properties:

- The main objective of an organic amendment is to assure the addition of organic matter to soil. **Organic matter** content is thus the main indicator that defines the status of soil amendment according to the European Committee for Standardization (AFNOR: FD CR 13456 2001).
- The quantity of organic matter brought to soil is a major characteristic but the composition of this organic matter is also relevant (Teglia et al., 2011). **Carbon and nitrogen** are the most important constituents of any organic material (Jenkinson et al. 1990; Michalzik et al. 2001). Their relative ratios with respect to their respective mineral and organic forms will influence their agronomic use (Havlin et al. 1990).
- Measuring the **carbon mineralization** through soil incubation test is also an effective way to assess the degradability of the carbon over time and its potential carbon sequestration in the soil.

As previously mentioned, the waste management processes applied will define the future soil application of the subsequent by-products (*i.e.* fertilizers, soil amenders). Generally, solid digestates with high organic matter content are preferred as soil amenders, while liquid digestates with important mineral fractions have a higher potential for application as fertilizer (Nkoa, 2013). The restoration of soil properties (soil structure, soil fertility, microbial activity) partly depends on the storage of the carbon brought to the soil through organic matter. Mineralization test is a pertinent indicator of the organic matter decomposition rate and consequently on the future carbon sequestration to soil (Hartz; et al., 2000; Lashermes et al., 2009; Teglia et al., 2010). Generally the C mineralization is decreasing in the following order: digestate > compost > biochar. According the C mineralization test, the main by-products (*i.e* digestate, compost, biochar) can be classified in three categories:

- Digestate with **still labile and partially stabilized** carbon (Albuquerque, 2012; Monlau et al., 2016). Indeed, the complete exhaustion of the most labile organic fraction during the anaerobic process, in order to obtain digestates with a high stability degree, is not easy to achieve at industrial level, the main objective of the anaerobic co-digestion being the biogas production (Albuquerque et al., 2012).
- Compost **with stable** carbon fraction. Composting in the aerobic degradation of organic matter and give to a stable organic matter and is generally applied on solid anaerobic digestate to improve its stability (Bustamante et al., 2012; Bustamante et al., 2013). Hartz et al., (2000) have investigated the C mineralization of various manure and subsequent compost samples. It was shown that C mineralization of manures averaged 35 % of the initial C content in 24 weeks whereas C mineralization of compost averaged only 14%.
- Biochar with **recalcitrant** carbon. Schouten et al., (2012) have investigated the carbon dynamics in soil of manure, its subsequent digestate and biochar. The highest losses of soil C from biological activity (CO₂ respiration) were observed in manure treatments (39% and 32% for loess and sandy soil), followed by digestate (31% and 18%), and biochar (15% and 7%).

Generally, digestates, apart from their fertilizing function, will also contribute to the short term turnover of organic matter in soils (Tambone et al., 2010). Compost due to a more stable organic matter will contribute to medium term soil organic turnover while biochar due to its high sequestration will contribute to long term sequestration (C sink in soil). Digestate gradually releases plant nutrients under microbial mineralization and its degradable organic matter is the primary source to start up the so called ecological “debris chain”. Conversely, pyrochar plays a role in carbon capturing and its long-term sequestration into the soil, thus contributing to climate change mitigation (Monlau et al., 2016). Recently, co-application

of biochars and other organic amendments has been determined to be an effective management practice for compensating the limitations of applying biochar and/or organic amendment and/or fertilizers alone (Rogovska et al., 2011; Qayyum et al., 2014).

Methodologies:

Organic matter will be determined according the European Norm NF EN 13039. The C and N content will be determined according protocol defined in the *NF U44-051* French Norm for digestate and compost. For biochar, methodologies to assess C and N content have been described in the European Biochar Certificate (EBC) and the IBI biochar standards methods. Carbon mineralization will be assessed according the protocol define in the *XPU 44-163* French Norm. Briefly, the agricultural soils is dried at room temperature and then sieved to 4 millimeters and stored in a cold room at 4 °C. Then, a dose of digestate on a selected agricultural soils is applied in a ballot at a load of 170 kg of nitrogen / ha on closed jars. A blank control with only the agricultural soil is also performed. In each jars, a small beaker containing (25 ml) of sodium hydroxide solution is set up in the bottom, with the objective to trap the CO₂ produced during the carbon mineralization. In parallel, in the bottom of each jars, 4 ml of distilled water is added to maintain humid atmosphere during the experiment. The jars are then hermetically sealed and installed in a thermostatic oven at 28 ° C. Every 3 days the jars were opened and the sodium hydroxide solution was assayed with 0.1 M HCl solution. During this operation, the ballots are removed from the jars and their mass is adjusted with water to reach the initial mass previously observed and thus maintain constant moisture content in the soil. The carbon content is dosed by a colorimetric method witch is detailed in the *XPU 44-163* French Norm.

AFNOR: *XPU 44-163 Organic soil improvers and growing media-Determination of potentially mineralisable carbon and nitrogen-Method of incubation under controlled conditions (2009).*

AFNOR: *NF U44-051 Amendements organiques—Dénominations spécifications et marquage (2006).*

EBC (2012) 'European Biochar Certificate - Guidelines for a Sustainable Production of Biochar.' European Biochar Foundation (EBC), Arbaz, Switzerland. <http://www.europeanbiochar.org/en/download>. Version 6.2E of 04th February 2016.

IBI Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in SoilInternational Biochar Initiative - May 2012.

NF EN 13039, *Amendements du sol et supports de culture - Détermination de la matière organique et des cendres.*

European Legislation

In France, standards NF U44-051 regulate the agricultural use as soil amendments (originating from wastes different than wastewater sludge that refers to the NF U44-095 norm) defining the compliance of chemical characteristics with limits of quality. French organic soil improvers must present dry matter content higher than 30 or 50% of the fresh weight according to the type of compost considered. Moreover, amendments must contain minimal organic matter content of 20% of fresh matter to be normalized according to French standards. French organic soil improvers shall also have a C/N higher than 8, except for sludge compost. Finally, the sum of mineral nitrogen (ammonium, nitrite, and nitrate) should be inferior to 1/3 of the total Nitrogen. In the German RAL GZ 251 quality label, digestates must present minimal organic matter content of 30% of dry matter (determined by loss on ignition) (Siebert, 2008).

As concerns for **biochar**; both the IBI and EBC have set value for the C content. For the EBC certificate, it is recommended a minimal carbon content of 50% (in dry basis). For the IBI a minimum carbon content of 10% (in dry basis) is recommended and three classes have been defined according the carbon content (class 1 > 60%; class 2 > 30 % and < 60%; class 3 >10 % and < 30%).

AFNOR: NF U44-051 Amendements organiques—Dénominations spécifications et marquage (2006).
 AFNOR: NF U44-095 Amendements organiques—Composts contenant des matières d'intérêts agronomiques, issus du traitement des eaux (2002).
 EBC (2012) 'European Biochar Certificate - Guidelines for a Sustainable Production of Biochar.' European Biochar Foundation (EBC), Arbaz, Switzerland. <http://www.europeanbiochar.org/en/download>. Version 6.2E of 04th February 2016.
 IBI Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil International Biochar Initiative - May 2012.
 Siebert, S.: Quality requirements and quality assurance of digestion residuals in Germany. In: ECN/ORBIT Workshop The future for Anaerobic Digestion of Organic Waste in Europe. N°remberg, Germany (2008).

• **Biodegradability and compostability of bioplastics**

Biodegradation and composting are processes in which molecular structure of materials is broken down through metabolic or enzymatic processes. The decomposition process occurs via enzymes secreted by naturally present or naturally occurring microorganisms (or microbes) such as bacteria, some fungi, etc. These microbes work alone or in colonies and play a vital role in our ecosystem. Biodegradation can occur in aerobic (requiring oxygen) or anaerobic (without oxygen) conditions. Biomass (humus) and biogas (carbon dioxide and methane) are the products of a biodegradation or composting process. Under aerobic conditions carbon dioxide is the primary gas emitted while in the case of anaerobic conditions methane is the primary gas.

These last decades, the development of bioplastics has attracted attention to the conventional plastics from petroleum compounds that can be responsible of environmental damage. Three types of composting conditions exist depending on they are conducted at the industrial scale or at home (high or ambient temperature), aerobic or anaerobic conditions. To define treatment routes that can valorize such products in their end-of life, three kind of biodegradability/compostability are considered:

1. packaging products that conform to the 'compostable' criteria of the aerobic degradation standard EN 13342 are suitable for composting (the tests simulate industrial scale composting conditions at high temperature),
2. those that conform to the anaerobic digestion criteria are suitable for that method of organic recovery (EN 14995) and
3. those that conform to the national "home compostable" standards at ambient temperature are suitable for composting nature in with others organic bio-wastes without any preliminary sorting.

Three types of composting conditions are recognized (**Table 2**) depending on how they are conducted at the industrial scale or at home (high or ambient temperature), under either aerobic or anaerobic conditions.

Table 2: Comparison of Industrial and Home Compostability.

	Industrial Composting: EN 13432 - 14995 Aerobic or anaerobic cond°	Home Composting: Vinçotte Certification Programme – NFT51-800
Biodegradation	Test performed at 58 °C +/- 2 °C, carbon dioxide at least 90 % compared with control within 6 months (approx 182 days)	Test performed at ambient temperature (20 - 30 °C), carbon dioxide at least 90 % compared with control within 365 days
Disintegration	Test performed at whatever temperatures are achieved in vessels, each at least 140 litre capacity. At maximum of 12 weeks (approx 84 days) no more than 10 % of original dry weight of test material > 2 mm.	Test performed at 20 - 30°C in vessels each at least 140 litre capacity. At maximum of 26 weeks (182 days) no more than 10 % of original dry weight of test material > 2 mm.

<p>Current certification and logos</p>		
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➤ **Aerobic degradation through industrial composting process**

Aerobic degradation in compost medium is considered as a potential option regarding the end of life treatment of bioplastics at the European level even if not yet widely exploited at the moment. This end of life option is expected to grow up over the coming years. Actually, even if a part of the carbon embodied in the bioplastic is emitted into air during composting, the remainder is stored as compost that can replace soil conditioners supporting humus formation. The main barrier to lift for this end of life option is about collecting, sorting, transporting and industrial composting plants processing. All these steps lead to energy consumption, specific logistic development, consumer awareness and additional carbon dioxide release, whose impact should be carefully weighted and compared to the expected benefit.

Methodologies:

By industrial composting...

Composting is an example of aerobic and biodegradation process resulting in the formation of gases mainly CO₂ and solid compost. There are several standards that can be used to certify that a material is compostable. The European standards EN 13432 (which refers to the compostability of packaging items) and EN 14995 (ascribed to the compostability of plastics in general) can be used to certify industrial compostability of plastic materials possibly used for packaging application but not only. To achieve certification, a material has to undergo testing at maximum 58°C for 180 days and has to biodegrade by 90% in absolute terms or relative to cellulose within that time frame. The threshold of 180 days maximum is intended to cover both biodegradation during the composting process as well as the biodegradation afterwards, during application of compost to soil.

The other requirements that the material has to fulfil according to these standards are i) a test of disintegration stipulating that at least 90% of the plastic size should be under 2 mm 12 weeks after starting composting ii) a test of ecotoxicity including seed germination and biomass production of two terrestrial plants grown up on the compost resulting from the material disintegration without any fertilizer addition (the growth should be 90% higher than that obtained with the control compost) iii) a maximal content of heavy metal and hazardous substances in the bioplastic material under testing.

The biodegradability of the selected materials will be assessed by conducting respirometric tests based on the measurement of the carbon dioxide release in aerobic conditions and composting conditions close to those used in municipal or industrial biological waste treatment facilities according to EN 13432 and EN 14995 standards.

DIN EN 13432 - Requirements for packaging recoverable through composting and biodegradation. Test scheme and evaluation criteria for the final acceptance of packaging.

DIN EN 14995 - Plastics - Evaluation of compostability - Test scheme and specifications. Broaden the scope to non-packaging plastics.

➤ Anaerobic degradation through anaerobic digestion process

The end of life is an important point on the sustainability of the bioplastics chain at the European level. Whereas the composting process is well known for the treatment of bioplastics at their end of life, no data have been reported until yet on the treatment of bioplastics by AD process. Anaerobic digestion process seems to be a promising valorization routes for bioplastics such as PHA (polyhydroxyalkanoates) to recover energy in the form of biogas or biomethane. Up to date, the methane potential is currently evaluated by the Biochemical Methane Potential (BMP) tests. Biomethane potential (BMP) tests, although routinely applied to measure the ultimate methane production (expressed in $\text{NL CH}_4 \text{ kg}^{-1} \text{ VS}$ or TS) from different organic materials (Holliger et al., 2016), has never been reported until yet on bioplastics wastes.

Methodologies:

By anaerobic digestion

Up to date, there is no European harmonization on the protocol of the Biochemical Methane Potential (BMP). As, no BMP protocol have been standardized currently, an adapted protocol will be used from recommendations of several publications (Angelidaki et al., 2009; OFEN, 2011) to assess the methane potential in wet anaerobic digestion process. In parallel, the biodegradation in dry anaerobic conditions is performed according to ISO15985:2004.

Angelidaki, M. Alves, D. Bolzonella, L. Borzacconi, J.L. Campos, A.J. Guwy, et al., *Defining the biomethane potential (BMP) of solid organic wastes and energy crops: a proposed protocol for batch assays*, *Water Sci. Technol.* 59 (2009) 927-934.

OFEN, 2011. *Optimisation des tests standardisés de digestibilité dans des réacteurs batch*.

ISO15985:2004 "Plastics –Determination of the ultimate anaerobic biodegradation and disintegration under high-solids anaerobic-digestion conditions -- Method by analysis of released biogas".

➤ Aerobic degradation in soil

For packaging materials, aerobic degradation in soil corresponds to a biodegradability in natural conditions and in domestic composting systems that does not require any sorting from other organic wastes, collecting and industrial plants composting steps unlike industrial aerobic composting. This end of life option is particularly relevant for bioplastic materials targeted for agricultural applications, even though they can be also collected and recycled. However, plastic materials are often thrown away in the environment or land filled and for this reason, their ability to i) be properly biodegraded in soil to avoid any accumulation and ii) ensure that they are safe for the soil ecosystem and environment should be taken into consideration. The release of biodegradable plastics in soil implies that two aspects are satisfied: full biodegradability to prevent any accumulation in soil and no ecotoxic effects on the soil ecosystem by the application of specific ecotoxicity tests conducted on plants, earthworms and aquatic organisms such as *Daphnia* or algae. Other bio-indicators could also be included to evaluate how the biodegradation of polymer in soil can impact the microbial nitrification potential, which can be considered as a relevant parameter for monitoring soil quality. The nitrification test procedure is derived from the International Standard ISO 14238.

Even if there is not yet standard specification of polymers in soil on ISO level, developments are ongoing at European level and consider a polymer to be completely biodegradable if 90% of the organic carbon present in the polymer can be converted to carbon dioxide within a period of maximum 2 years as required by the upcoming European standards or other standards such as "OK biodegradable soil" of Vinçotte and the two Italian standards UNI 11462 (2012) and UNI 11495 (2013). Actually, the 100% biodegradation rate is rarely reached due to the fact that the carbon dioxide is the only product of the reaction that can be assessed in the absence of reliable methods available to determine the biomass

and the by-products produced during the biodegradation process. In contrast, according to the NF 52001 French standard, full biodegradation in soil means that more than 70% of biodegradability relative to cellulose should be reached in one year. A threshold of 90% could appear as a very stringent requirement for bioplastic manufacturers but could however be reached by better selecting the polymers blend entering in the composition of the bioplastic films and optimizing their formulation and copolymerization.

Methodologies:

The measurement of biodegradation in soil will be carried out by using either NFT51-800 specifications or the analysis standard ISO/FDIS 17556. The test temperature will be set at 28°C. According to the recent specification standard PR NF EN 17033, the maximum test duration is 24 months and a mineralization value of 90% should be reached, this threshold being currently considered to be proof of complete biodegradation. Both raw materials and the finished products manufactured with these materials need to be tested. In addition to this first requirement, the material under testing and its components should have to satisfy a limited concentration of heavy metals (As, Cd, Cr, Cu, F, Hg, Ni, Mo, Pb, Se and Zn) and harmful organic compounds (polychlorinated biphenyl, fluoranthene derivatives and benzopyrene). Finally, ecotoxicity tests will be undertaken on soil samples where the bioplastic material added at a concentration of 1% in mass has been degraded for 3 months will be performed. The objective of these test will be to verify the absence of ecotoxicity towards i) plants evidenced by no negative effect on the seed germination and growth of plants, ii) earthworms indicating no lethal effect on *Eisenia fetida* due to a potential acute toxicity and iii) algae or Daphnia revealing no inhibition of the growth possibly related to a chronic toxicity.

ISO/FDIS 17556 Plastics — Determination of the ultimate aerobic biodegradability of plastic materials in soil by measuring the oxygen demand in a respirometer or the amount of carbon dioxide evolved.

PR NF EN 17033 - Plastics - Biodegradable mulch films for use in agriculture and horticulture - Requirements and test methods (Octobre 2016).

NF T 51-800 Plastics - Specifications for plastics suitable for home composting.

Vinçotte, 2007. Program OK2 e home compostability of products. Specification OK compost home: initial acceptance tests, Vinçotte, <http://www.okcompost.be/>.

• Physical-chemical properties

➤ pH

The **pH** of soil is one of the most studied parameters because it reflects the ionic balance between the water and the solid components of the soil. Soil pH influences the solubility of nutrients, but it also affects the activity of microorganisms responsible for breaking down organic matter and most chemical transformations in the soil. Furthermore, the addition on the soil of by-products can significantly affect the soil pH and it is thus an important indicator to be monitored. There are several methods of pH measure for a sample of soil put in suspension. These methods differ according to the nature of the solution and the solid / liquid ratio. The pH (H₂O) is the most commonly used and seasonal variations can be detected.

Methodologies:

The soil pH is measured according to the standard ISO 10390:2005 on air-dried soil samples (fraction < 2 mm). The pH of the soil is potentiometrically measured in the supernatant suspension of 1:5 (volume fraction). This liquid is made up of distilled/deionized water. Take a representative sample (at least a volume of 5 ml) of the air-dried soil. Place the test sample in the sample bottle with cap (50ml) and add five times its volume of solvent. Shake or mix the suspension for 15 min, using the mechanical shaker or mixer, and wait for at least for 1 hour before measuring but not longer than 3 hours. Ingress of air during standing after shaking should be avoided. Measure the pH in the suspension at 20°C ± 2°C

immediately after being stirred. The stirring should be at such a rate to achieve a reasonable homogeneous suspension of the soil particles, but entrainment of air should be avoided. Read the pH after stabilization of the value is reached.

ISO 10390 (2005). *Soil quality – Determination of pH*

➤ Water Holding Capacity (WHC)

The **water holding capacity** (WHC) of a soil is a very important agronomic characteristic. Available water is the difference between field capacity which is the maximum amount of water the soil can hold and wilting point where the plant can no longer extract water from the soil. However, as noticed by Blazka and Fischer (2014) in the introduction of their paper, there is no consensus on the definition and utility of WHC. We can retain that water holding capacity (WHC) is defined as the amount [g] of water per g dry soil retained against gravity when water is in excess. Soil water holding capacity is controlled primarily by the soil texture and the soil organic matter content. In general, the higher the percentage of silt and clay, the higher the water holding capacity because these particles have a much larger surface area than the sand particles. However, this does not mean that water is easily available for plants. Indeed, the abundance of clay can favor small pores which make plants to struggle against a greater effect of suction. The water holding capacity also increases as the level of organic matter increases in a soil, due to the affinity of organic matter for water but also by its effect on creating and stabilizing soil pores. For this purpose, the supplying of by-products (*i.e.* biochar, compost and digestate) can directly affect the WHC of soil.

Addition of biochar, compost or digestate have been largely tested in order to improve soil properties including WHC. Organic amendments generally increase WHC and biochar has a high capacity to retain water due to high amount of small pores (Major et al., 2009). The incorporated biochar particles could change the pore-size, increase pore connectivity, improve the soil structure, and finally the soil's water holding capability (Asai et al., 2009; Jien and Wang, 2013; Liu et al., 2016). Moreover, biochars present also larger pores which let a heavy rain flow through from topsoil to deeper soil layers (Asai et al., 2009). Mohamed et al. (2016) showed that incorporation of biochar could increase WHC by 21 to 60 % and this phenomenon was enhanced after 6 weeks incubation by 12 to 60%. Many works concluded that an incubation period would cause surface oxidation of biochar reducing hydrophobicity and leading to a better water retention. In contrast, column experiments where biochar was added to sandy soil showed that WHC was simply maintained in the course of 90 days while WHC decreased gradually in the control soil (Basso et al., 2013).

Biochar impact on WHC is also affected by the amount of organic matter present in the soil. Abel et al. (2013) found that water retention increased for sandy sites with low organic matter content while for the soil with high organic matter content, which initially possesses a higher WHC, no increase was detected. For loamy soils, WHC was moderately improved by 11% (Karhu et al., 2011) and up to 15% (Laird et al., 2010). However, Wang et al. (2016a) showed in a pot experiment that the addition of pine biochar significantly increased soil water availability but not plant growth. The use of pine biochar enriched with nutrients improved the plant growth demonstrating vegetation performance was driven by nutrient availability from biochar rather than its water holding capacity.

On the contrary, the effects of compost or digestate on the WHC have been less investigated. A sandy loam soil receiving manure and sewage sludge composts showed, after 2 lettuce crops, a higher WHC (approximately 12-24% more) than the soil treated only with inorganic fertilization (Hernandez et al., 2016). Liu et al. (2012) mentioned that a biochar-compost mixture doubled water capacity of sandy soils in Germany. In a field experiment, Wang et al. (2016b) compared impact of diverse treatments with corn stalk biochar and/or pig manure compost incorporated to a sandy loam soil: only the mixture of biochar (at the highest load) + compost increased the WHC by 5,4%. However, crop performance was also

evaluated and biomass of mung bean was higher at medium growing phase for every amendment (single or in mixture) while it was higher at harvest time only for the 2 biochar/compost mixtures tested. Effects of digestate spreading on soil physical properties are scarcely reported. Nkoa (2013) indicated that few studies would show a positive impact on moisture retention capacity. Another work demonstrated an increase of 42% and 57% in the WHC after pyrolysis of two solid digestates explained by the increase of both accessible surface area and porosity (Monlau et al., 2016).

Methodologies:

A gravimetric method frequently used in Europe places the saturated soil sample into a cylinder bottom closed by a water porous membrane. The excess water is drawn away by gravity. Once equilibrium is reached, the water holding capacity is calculated based on the weight of the water held in the sample vs. the sample dry weight.

The soil sample is dried at 40°C in order to avoid texture changes in oven. The soil is placed in the cylinder and is tapped 15-20 times on a table by letting it fall from a height of about 2-3 cm. This tapping is assumed to produce the same packing effect as it naturally occurs in the field, even though this assumption is not strictly correct. Cylinder with dry soil is weighed. The cylinder filled with soil is put into a pan with a few centimeters of water to allow the soil to become saturated from the bottom to the surface. The cylinder is then removed from the pan of water and suspended until drainage is complete. It is better to do this in a humid enclosure to avoid water loss by evaporation. Cylinder with moistened soil is weighed.

Water Holding Capacity is calculated as
$$\frac{\text{mass of moistend soil} - \text{mass of dry soil}}{\text{mass of dry soil}} \times 100$$

➤ Bulk density

The soil bulk density, is the weight of dry soil divided by total soil volume. The total volume of soil consist of pores volume (air and water) plus solids volume. Bulk density provides indication on solids grains arrangement and soil structure. Bulk density is commonly used to investigate compaction of layers by agricultural practices. It allows estimating the soil permeability, the capacity of exchanges between the ground, the water and the atmosphere. Thus potential root development can be evaluated. Bulk density is used to determine various nutrient levels and other soil quality indicators on an area basis, by converting weight measurements (e.g. mg/kg) to area measurements (e.g. kg/ha).

Use of biochars as soil conditioner/amendment has been widely studied. The bulk density of biochars typically ranges between 0.09 and 0.5 g cm⁻³ as reported by Lehman et al. (2011). And these values, much lower than those of soils, contribute to lower their bulk density after adding biochar (Oguntunde et al., 2008; Laird et al., 2010; Peake et al., 2014). However biochar impact on bulk density depends on the soil texture, on the feedstocks form which the biochar is originating and on the operational conditions of the thermochemical processes. For instance, Quin et al. (2014) found that biochar made from woody residues had a greater effect on bulk density in a coarse-textured soil than in soils with higher clay content. The wheat straw biochar tested appeared to decrease bulk density of the Planosol slightly more than a woodchip and 2 vineyard-pruning biochars. Solid organic municipal waste can be also used to produce biochars. Randolph et al. (2017) studied effect on soil parameters of biochars addition prepared from newspaper, cardboard, woodchips and landscaping residues. They showed that the bulk density and soil aggregate stability were improved by the addition of biochar at the lower concentrations, especially by biochars from woodchip, plant residues and cardboard.

Effect of compost on soil parameters and bulk density has been also frequently studied. A ten years' experiment showed that the use of a vegetal compost resulted in a better decrease in bulk density (-19.5%, -22.1%) compared to a mineral fertilizer application (-11.6%, -13%) (Herencia et al., 2011). Celik

et al. (2010) didn't observe any improvement of bulk density by mineral fertilizer treatment but application of vegetal compost led to a bulk density decrease (-17.8%, -20.6%) better than the one obtained with a cattle manure (-10.9%, -14.2%). In order to restore compacted roadside soils for tree plantings, the addition of compost derived from food and yard waste, at 10-50% v/v incorporation rates, lowered the bulk density of the test soils compared to their initial density (McGrath et al., 2016).

Contrary to biochar and compost, very few is reported concerning how digestate impacts the bulk density. One field experiment by Garg et al. (2005) showed that liquid digestate from agricultural waste reduced bulk density. Nkoa (2013) suggested that cellulose, lignin and humic substances, present in particular in solid digestate could act to decrease bulk density.

Methodologies

The most common method of measuring soil BD is collecting a known volume of soil using a metal cylinder pressed into the soil (intact core), and determining the weight after oven drying at 105°C. This method works best for moist soils. Manually pre-wetting the soil will not affect the bulk density. The standard ISO 11272:2017 specifies three methods for the determination of dry bulk density of soils calculated from the mass and the volume of a soil sample. The latter is either known (core method) or determined (excavation method and clod method).

ISO 11272:2017 Soil quality - Determination of dry bulk density

➤ Cation exchange capacity (CEC)

Cation exchange capacity (CEC) is the total capacity of a soil to hold exchangeable cations. It is an important soil parameter because it influences nutrient availability to plants, pH and structure stability of soils. The main ions associated with CEC in soils are the exchangeable cations: Ca^{2+} , Mg^{2+} , Na^{+} and K^{+} which are generally referred to as the base cations (Rayment and Higginson 1992). However for acidic soils, the most prevalent cations are H^{+} , Al^{3+} and Mn^{2+} which constitute the "exchangeable acidity". Exchange and leaching are easy at low CEC while this is difficult with high CEC.

In soils, organic matter (humic acids) and clay minerals are negatively charged on their surfaces. They hold positively charged ions but these cations are only for a moment fixed and remain exchangeable and available for the plants. The complex interactions of the permanent and variable electric charges limit the variations of the pH under the influence of the chemical and biological factors conferring it its buffering capacity. The lower the CEC of a soil, the faster the soil pH will decrease with time. When ions concentration decrease in water stored in soil porosity, the adsorbing complex frees ions to rebalance the system: this is a dynamic equilibrium. Because a higher CEC usually indicates more clay and organic matter is present in the soil, high CEC soils generally have greater water holding capacity than low CEC soils. Furthermore the increase of the CEC in soils besides to improve the fertilizers properties will also improve contaminants and nutrients retention avoiding leaching to groundwater (Novoa-Munoz et al., 2008; Lehman et al., 2009; Major et al., 2010).

Determination of cation exchange capacity (CEC) is highly recommended to organic products (*i.e.* digestate, biochar, compost...) when they are used as growing media (Teglia et al., 2011). CEC will determine a substrate ability to absorb specific cations (Ca, Mg, K, Na...) and can be used as a maturity indicator as it rises during aerobic biological treatment along with organic matter reorganization and humification processes (Teglia et al., 2011).

The CEC varies generally from less than 8 cmol (+)/kg (sandy soil, poor in organic matter) to more than 25 cmol (+)/kg (clayey soil and/or rich in organic matter). Since several years numerous studies measure the effects of organic soil improvers on the CEC and the fertility of soils. It is in particular the case of

biochars and composts but very little is reported about digestate spreading (Prost et al., 2013; Peng et al., 2011; Liang et al., 2006; Sáez et al., 2017).

Methodologies

There are several methods to measure CEC. They differ essentially by the pH of extraction and by the nature of the reagent. In the NoAW project, the CEC Metson at pH of 7 will be used.

Methods at given pH: CEC Metson at pH7: It is the measure of CEC with an extraction at pH 7 by ammonium acetate 1N. She allows the measure of the potential negative charge of the soil at pH 7. CEC Metson is well correlated with the quantity of clay and organic matter. Advantage: Method of reference used for a very long time by numerous laboratories. Inconvenience: It should not be confused with the effective CEC measured at the soil pH. Generally, the CEC Metson provides higher values than effective CEC for acidic soils and lower values for basic soils.

4.3.1.2 Innocuity parameters

Compost, digestate and biochar can have a positive effect on physical, chemical, and biological soil parameters due to their amending and/or fertilizers value but can exert also negative effect due to contaminant (organic and inorganic) or pathogens introduction in soil. Organic pollutants are unwanted chemical compounds supplied through the feedstocks (wastes) or generated during the wastes management processes. However, little is known about the concentration, and transformation of persistent organic pollutants during biological and thermochemical processes that could further persist in the final products such as digestate, compost and biochar representing an environmental and human burden (Kusmierz and Oleszczuk, 2014). Heavy metals and pathogens are also important parameters to be monitored in organic by-products to avoid any detrimental effect in soil properties. The various indicators of innocuity that will be assessed during the NoAW project are described in Table 3. Besides classical contaminants and pathogens, a specific attention will be paid on emergent contaminants like veterinary, pesticides and pharmaceutical compounds.

Table 3. Innocuity parameters recommended assessing for the environmental sustainability evaluation of the wastes management processes developed on the soil item.

Indicators names	Description	Units or Parameters quantified
Heavy metals	Determination of the main trace elements that could have a negative impact on the soil and micro-organisms. Among them As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Se, Zn	mg / kg Dry Matter
Pharmaceuticals (veterinary drugs)	Determination of veterinary antibiotics and their metabolites	mg or ng / kg TS
Pesticides	Determination of the pesticides content	mg or ng / kg TS
Estrogenic compounds	Determination of natural and conjugated estrogens	mg or ng / kg TS

Organic trace compounds	Determination of Polycyclic Aromatic Hydrocarbons (PAHs) Polychlorinated biphenyls (PCBs) and dioxins	mg or ng / kg TS
Polyphenols	Determination of the total polyphenols content	mg / kg TS
Inert	Determination of the inert (plastic, glass, metals, etc.) in wastes stream products	g _{inert} / kg dry matter
Pathogens	Determination of pathogens in bioenergy wastes streams (digestate, compost): Clostridium perfringens sp.; E. Coli; Salmonella, enterovirus, helminth eggs.	CFU / g Raw Matter

• Pathogens

For a very long time manures were spread on farmlands as amendments. More recently composts and biogas plants digestates were also used resulting from the processing of different residues: manures, industrial or municipal biowastes, sewage sludges. All those animal by-products contain a great load of microorganisms and among them various bacterial, fungal, viral, and parasitic and prion pathogens. Their presence implies a potential health problem and the need to control the waste entering the process as well as the obtained products. In Europe, as in the USA and other countries, there are laws which impose rules of pathogen monitoring for animal by-products and treatment processes before organic amendment application to agricultural lands. For more than 20 years, numerous studies have been trying to assess the evolution of pathogens in biowaste and during the processes of composting and anaerobic digestion. It should be noted that the use of biochars as amendment is not a concern for health as the temperatures of organic matter pyrolysis sterilize those biowastes.

In a not exhaustive way, it has been widely documented that E. coli, enterococci, Salmonella, Staphylococcus could be attenuated by 60 to 85% during composting of diverse biowastes: Chicken litter (Mohee et al., 2008), bovine manure (Millner et al., 2014), winery and distillery wastes (Bustamante et al., 2008) and the achievement of a temperature >60°C were essential conditions. Other pathogens like nematodes, viruses or Clostridium were less studied. (Pourcher et al., 2005) showed the hygienic effect of sludge compost in mixture with straw; this resulted in a significant reduction of enteric microorganisms and Clostridium by 4 and 2 Log units respectively. The concentrations of Salmonella, enteroviruses and viable nematode eggs in the final product were not detectable. Beyond the temperature, factors as exposure time, moisture content, windrow turning conditions and local microbiota can also influence the compost hygienisation. For a few years, it has been demonstrated that anaerobic digestion is able to decrease pathogen numbers, under mesophilic conditions (35-39°C) the most common ones, and more efficiently under thermophilic conditions (above 50°C) (Franke-Whittle and Insam, 2013). As evidenced by Dahab and Surampalli (2002) or Gantzer et al. (2001) Salmonella could persist at weak concentration (less than 100 /g) with 3-5 order of magnitudes less than as fecal coliforms, fecal streptococci and enterococci. Viruses are inactivated during AD, but the rate of inactivation is dependent on the virus, the temperature and the duration of digestion (Monteith et al., 1986; Spillman et al., 1987; Gao 2013). Olsen and Larsen (1987) observed that the spores of Clostridium perfringens were not inactivated, neither by mesophilic nor by thermophilic anaerobic digestion and ever since that has been confirmed by almost all experiments.

In digestates stored at 24°C during 40 days, Maynaud et al. (2016) showed the persistence of L. monocytogenes, detected up to 20 days after inoculation, was higher than that of Salmonella enterica Derby,

detected for 7– 20 days, and of *Campylobacter coli* (not detected after 7 days). Quantification by qPCR suggested a potential loss of culturability and induction of viable but non-culturable state which could be the underlying mechanism for the regrowth of pathogens. In contrast to gram-negative *E. coli* and *Salmonella* *Clostridium perfringens* produces spores as survival strategy. So, a longer persistence for these bacteria than for the other bacteria can be assumed. Regrowth of pathogens and their spores can also occur in storage facilities (Sidhu et al. 2001; Pepper et al. 2006). Stabilization and pathogens' attenuation of output digestates can be achieved through post-treatment as pasteurization and composting.

If many studies are interested in the evolution of the pathogens and microbial indicators in the sludges, composts and digestates (with regard to regulation aims), few papers report the fate of pathogens in the soil after amendment spreading. Pourcher et al. (2007) showed different microbial behavior after sewage sludge application at 15cm depth into a sandy soil: enteroviruses were undetectable in 2 weeks, fecal indicators decreased up to 1.8 Log₁₀ units over 2 months and spores of *C. perfringens* remained stable. Environmental factors as soil moisture, pH and temperature influence the survival of fecal bacteria in soil. Goberna et al. (2011) tested 6 experimental treatments resulted from the combination of three types of amendments (none, cattle manure and digestate) to both γ -sterilized and non-sterilized soils. Manure anaerobic digestion eliminated cultivable *Escherichia coli* and *Salmonella*, and *Listeria* was reduced by one order of magnitude. The authors assumed that the indigenous microbiota suppressed the proliferation of pathogens in soil over 3 months after the application.

Methodologies:

For pathogens analysis, the following ones will be investigated during the NoAW Project: *Clostridium perfringens* sp.; *E. Coli*; *Salmonella*, enterovirus, helminth eggs. The protocols that will be used have been adapted from the CEN /TC 308. More details of protocol will be described by the VERMICOM partner during the implementation of the pathogens analysis in the WP3 and WP4.

CEN /TC 308 – doc525.2001 Revision of Directive 86/278/EEC (3rd Draft).

European legislation

European animal by-products regulation no. 1069/2009. Limits: *Salmonella*: <1 CFU / 50 g; *E coli*: < 500 CFU/ g; *Clostridium perfringens* spores: significant reduction by treatment; Enteroviruses: < 1 / g; helminth eggs: < 1 / g.

Regulation (EC) No 1069/2009 of the European Parliament and of the Council of 21 October 2009 laying down health rules as regards animal by-products and derived products not intended for human consumption

• Heavy metals

The Waste Framework Directive (2008/98/EC), among other amendments introduces a new procedure for defining end-of-waste criteria, which are criteria that a given waste stream has to fulfil in order to cease to be waste. In the technical proposal “End-of-waste criteria for biodegradable waste subjected to biological treatment (compost & digestate)” (JRC, 2014), heavy metals are one of the listed parameters for assurance of compost and digestate quality from environmental or human health point of views. Indeed, if composts are applied to land, their chemical content could be transferred to the soil.

The fate of the heavy metals in soil is very site specific and depends on a number of factors such as the type and pH of the soil. Therefore, there are important local variations concerning the accumulation of heavy metals, their leachability into groundwater, and the uptake of heavy metals by plants and consequences once in the food chain (JRC, 2014).

Solubility and availability of heavy metals are usually decreasing during anaerobic digestion (Insam et al., 2015), mainly due to precipitation processes with sulfide, carbonate and phosphate (Möller & Müller,

2012). Decrease of Cd, Zn and Mg has been attributed to sulfide and struvite production (Zirkler et al., 2014). The formation of precipitates, however, does not mean that the total heavy metal contents decrease, if not a solid/liquid fractionation is performed and thus heavy metal contents are enriched in the solid phase. Massé et al. (2007) found that 18.4% of Zn and 41.4% of Cu have remained in swine manure biodigesters. While a decrease in heavy metal availability has been shown in pot experiments, no such evidence has been found in field experiments (Möller & Müller, 2012).

Biochar is able to very effectively bind a number of heavy metals, thereby immobilising them for a long period of time. However, as the amounts of biochar used in agriculture are relatively low compared to those of compost and manure, toxic accumulation of heavy metals could practically be ruled out, even when thresholds are higher (EBC, 2012). Nevertheless, this is no sufficient reason to disregard the heavy metal thresholds stipulated in Germany's Soil Protection Act or Switzerland's Chemical Risk Reduction Act, or any other European legislation.

Methodologies:

For heavy metals determination, inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Insam et al., 2015), also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES) is the most used technique. However, with ICP coupled to mass spectrometry (ICP-MS) is often preferred (Govasmark et al., 2011). Therefore, after microwave-assisted HNO₃ digestion, ICP-OES and/or ICP-MS analyses will be performed (for biochar, see also <http://www.european-biochar.org/en/analytical%20methods>).

EBC (2012) 'European Biochar Certificate - Guidelines for a Sustainable Production of Biochar.' European Biochar Foundation (EBC), Arbuz, Switzerland. <http://www.europeanbiochar.org/en/download>. Version 6.2E of 04th February 2016
Govasmark E., Ståb J., Holen B., Hoornstra D., Nesbakk T., Salkinoja-Salonen M. 2011. Chemical and microbiological hazards associated with recycling of anaerobic digested residue intended for agricultural use. Waste Manag. 31, 2577–2583
Insam H., Gómez-Brandón M., Ascher J. 2015. Manure-based biogas fermentation residues e Friend or foe of soil fertility? Soil Biol. Biochem. 84, 1-14

European legislation

Limits are usually set at a national level and differ from country to country (JRC, 2014). At the EU level, a set of heavy metal concentration limits exists as part of the EU eco-label criteria for soil improvers and growing media. Another set of limits applies to the use of certain composts in organic agriculture. In the End-of-waste criteria proposals (JRC, 2014), a comparison of digestate quality assurance systems in Europe is reported. Considering heavy metals in digestates, for Belgium (Flanders) (BE, FL), Switzerland (CH), Germany (DE), Sweden (SE), and United Kingdom (UK), the limits referred to mg/kg dry matter range: As 150 (BE, FL); Cd 1-6; Cr 70-250; Cu 100-600; Hg 1-5; Ni 30-50; Pb 100-300; Zn 400-900.

In the same document, Annex 3 (pp. 225-227), heavy metal limits in European compost and digestate standards are reported. The proposed content of heavy metals for compost and digestate (JCR, 2014), referred to mg/kg dry weight are: Cd 1.5; Cr 100; Cu 200; Hg 1; Ni 50; Pb 120; Zn 600.

Regarding to biochar, the following maximum values for heavy metals, corresponding - for the basic quality grade – to Germany's Federal Soil Protection Act (Bundes-Bodenschutzverordnung or BBodSchV), and - for the premium quality grade - to Switzerland's Chemical Risk Reduction Act (Schweizerische Chemikalien-Risikoreduktions-Verordnung or ChemRRV) (EBC, 2012). The thresholds refer to the biochar's total dry matter, and are, for premium and basic, respectively: Pb < 120 and < 150 g/t; Cd < 1 and < 1.5 g/t; Cu < 100 g/t (for both); Ni < 30 and < 50 g/t; Hg < 1 g/t (for both); Zn < 400 g/t (for both); Cr < 80 and < 90 g/t; As < 13 g/t TM (for both). The IBI Biochar standards (2012)

have also set some maximum allowed threshold level for heavy metals: As: 12-100 g/t; Cd: 1.4-39 g/t; Cr: 64-1200 g/t; Co: 40-150 g/t; Cu: 63-1500 g/t; Pb: 70-500 g/t; Hg: 1-17 g/t; Mo: 5-20 g/t; Ni 47-600 g/t; Se: 2-36 g/t; Zn: 200-7000 g/t.

As for bioplastics, the NF EN 13432 have defined heavy metals threshold value for biodegradable packaging expressed in mg kg⁻¹ DM. Zn : 150; Cr : 50 ; Cu : 50 ; Mo : 1 ; Ni : 25 ; Se : 0.75 ; Cd : 0,5 ; As : 5 ; Pb : 50 ; F : 100 ; Hg : 0.5.

Joint Research Centre (JRC), European Commission. 2014. End-of-waste criteria for biodegradable waste subjected to biological treatment (compost & digestate): Technical proposals, Final report, December 2013, Sevilla, Spain. doi:10.2791/6295

EBC (2012) 'European Biochar Certificate - Guidelines for a Sustainable Production of Biochar.' European Biochar Foundation (EBC), Arbaz, Switzerland. <http://www.europeanbiochar.org/en/download>. Version 6.2E of 04th February 2016

IBI Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil International Biochar Initiative - May 2012.

DIN EN 13432 - Requirements for packaging recoverable through composting and biodegradation. Test scheme and evaluation criteria for the final acceptance of packaging.

• Pesticides

Most substrates used for biomethanisation will have levels of organic contaminants that are low enough for not inhibiting the process. However, if not sufficiently degraded in the anaerobic digestion process, they can render the digestate unsuited as a fertilizer and impair soil health (Insam et al., 2015). Among these organic contaminants, there are the pesticides. In the End-of-waste criteria for biodegradable waste subjected to biological treatment (compost & digestate) technical proposals (JRC, 2014), pesticides are described as one of the measured parameters in the FATE-COMES study. In 2014, the total quantity of pesticide sales in the EU-28 amounted to close to 400 000 tons. Spain (19.9 %), France (19.0 %), Italy (16.2 %), Germany (11.6 %) and Poland (5.9 %) were the Member States in which the highest quantities of pesticides were sold (Eurostat, 2016). In the EU-28, fungicides and bactericides are the most sold group of pesticides, followed by herbicides.

During JRC Sampling and Analysis campaign, 54 samples were screened for several pesticides (JRC, 2014). The sum of the concentrations for the most used 7 pesticides was in all cases < 50.1 µg/kg. For chlorophenols, on 29 samples, the highest detected concentration was 0.08 mg/kg. Brändli et al. (2007c) carried out a survey on 13 compost and 5 digestate samples from commercial plants in Switzerland. Out of the 269 analysed pesticides, 30 fungicides, 14 herbicides, 8 insecticides, and 1 acaricide were detected in compost and digestate. The consumption data on pesticide use available for Switzerland was not reflected in compost, whereas the pesticide half-life in soil seemed to be related to their occurrence. Fungicides, in particular triazoles, dominated over the other pesticides, not only in terms of incidence of detection, but also of concentrations. Difenoconazole, fenbuconazole, propiconazole, and tebuconazole were detected in all compost samples. These compounds are widely used in viticulture, orchards and horticulture in Switzerland and other countries. They are frequently detected in fruit and vegetables and some of them show half-life of more than 40 days in soil. Compost and digestate did not differ in fungicide concentrations. The sum of all fungicides was significantly higher in urban composts and digestates containing organic kitchen waste (median: 61 mg/kg dry matter, d.m.) compared with rural green waste compost (median: 27 mg/kg d.m.). In general, numbers and concentrations of fungicides detected in compost decreased with the duration of the composting process. The lower abundance of herbicides compared with fungicides in compost can be explained by the fact that herbicides are mainly used at the beginning of the growing season in horticulture and should be mostly degraded by the time of harvest. In contrast, fungicides are applied later during the growth season, or for post-harvest treatment. There was no difference in herbicide concentration in compost and digestate. The median

concentration of the sum of all insecticides was 4.1 mg/kg dw ($n = 18$). The only insecticide detected in several composts was propoxur (median 4.2 mg kg/1 dw, $n = 12$). In contrast to former studies, organochlorine insecticides were not detected in composts and digestates.

In another study (Kupper et al., 2008) concentration levels and dissipation of pesticides during composting and digestion at full-scale plants were followed. 28/271 analyzed pesticides were detected. Total concentrations were 36-101 mg/kg dw in input materials and 8-20 mg/kg dw in composts after 112 days of treatment. Also in this case, fungicides and among them triazoles clearly dominated over other pesticides. More than two-thirds of all pesticides detected in the input materials showed dissipation rates higher than 50% during composting, whilst levels of most triazoles decreased slightly or remained unchanged. The investigation on semi-dry thermophilic anaerobic digestion suggests that pesticides preferentially end up in press water after solid-liquid separation.

Govasmark et al. (2011) detected only 11/250 pesticides analyzed (10 fungicides and 1 insecticide, methoxychlor), but only imazalil (<0.30–5.77 mg/kg dw) and thiabendazol (<0.14–0.73 mg/kg dw) were frequently detected in the AD residue-fiber.

The carbonaceous material from anaerobic pyrolysis has been demonstrated to have potential to mitigate the pesticides contaminations in soil and water substrates. The production variables including the feedstock type and the process conditions have direct effect on biochar properties (Yavari et al., 2015). The combination of the variables provides a wide diversity of biochars with different characteristics each proper for particular use. There is the possibility to produce designed biochars with high removal ability for pesticides through optimizing the production factors. Based on the literatures, the highest treatment temperature, heating rate, gas pressure, and retention time sequentially are the main pyrolysis variables which determine the biochars sorptive properties. However, their impacts on different feedstock are not the same, as different biomasses are unlike in composition, structure, and consequently in reaction and resistance against heat and gas pressure. Therefore, the evaluation of different feedstock under varying pyrolytic parameters and the optimization of the condition for each feedstock can help to adjust the biochars characteristics and maximize their sorption capacity. In addition to biochar properties, the environmental conditions, pesticides nature, contact time between biochar and the matrix, the biochar aging, and stability can significantly influence the sorption process and can contribute to increase its complexity. When applied to the soil or water, a biochar, can present different performance based on the substrate properties. This can happen similarly in the relation to the pesticides type. Biochars show different affinity for a specific organic contaminant based on the polarity and ionizability of the chemical.

There is still limited knowledge on how biochar influences immobilization of polar pesticides in agricultural soils. Yavari et al. (2016) found that addition of biochars to the soils (1% (w/w)) could enhance polar herbicides sorption. The extent of the effects, however, was found to be different in various biochars and herbicides. Pyrolysis temperature and type of biomass were found to have major impacts on sorption capacity of the biochars. Lower conversion temperature (300 °C) increased materials surface functional groups, making biochars more efficient in sorption of polar molecules. It can be concluded that the biochars sorption properties were directly controlled by production variables (feedstock kind and pyrolysis temperature) and the sorption mechanisms were determined based on the physicochemical characteristics (polarity, hydrophilicity and ionizability) of the sorbate molecules.

It has been recognized that the presence of biochar in soil not only enhances the sorption of different pesticides, but also affects the nature of sorption mechanisms and the bioavailability of pesticide residues for living organisms. Moreover, the application of biochar in agricultural soil next to lakes or bodies of water may effectively reduce the contamination of underground water by decreasing the leaching of applied pesticides (Safaei Khorram et al., 2016).

Methodologies:

For pesticide analysis, gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-tandem mass spectrometry (LC-MS/MS) are the two techniques of choice, depending on investigated pesticide chemical class. For extraction from water samples, see, for example, Di Corcia et al. (2000). Briefly, water samples will be directly extracted by solid phase extraction (SPE) using graphitized black carbon as adsorbent material. Soil samples will be first treated with acetonitrile or another suitable solvent, diluted in water and passed on the SPE column. Determination will be carried out by LC-(high resolution) MS/MS.

European legislation

No specific legislation exists in Member States for these compounds in composts or digestates, but Austria has a limit value of 500 µg/kg for the sum of 10 organochlorine pesticides (JRC, 2014).

Joint Research Centre (JRC), European Commission. 2014. End-of-waste criteria for biodegradable waste subjected to biological treatment (compost & digestate): Technical proposals, Final report, December 2013, Sevilla, Spain. doi:10.2791/6295.

• Veterinary compounds

The contamination of both the terrestrial and the aquatic environments with organic micropollutants, such as veterinary pharmaceuticals, has aroused attention in the course of the last decades (Burke et al., 2016). The application of polluted manure to agricultural soils is the main contamination source for veterinary pharmaceuticals, in particular antimicrobials (including both natural antibiotics and synthetic antibacterial compounds); a second contamination source is the direct excretion to soils. It has been estimated that the loads of antibiotics shed by manuring are to kilograms per hectare (Kemper, 2008). Then, through surface runoff and percolation, these veterinary pharmaceuticals may enter both surface water and, to a lesser extent, groundwater, respectively (Burke et al., 2016). The matter of concern for these compounds is not only their potential long-term toxicity, but mostly their contribution to antibiotic resistance. Veterinary pharmaceuticals entering the environment via contaminated manure can be into various forms: unchanged, transformed, or metabolized, i.e., conjugated to polar molecules; moreover, they can be subject to degradation, sorption, plant uptake, or transport processes. For instance, some antibiotics are transformed to conjugates such as acetylated metabolites, becoming inactive and analytically camouflaged, but in manure the acetyl group can be cleaved, releasing the original active ingredient (Kemper, 2008).

Chemical and physical behavior in the soil depends on the molecular structure of the pharmaceutical (Kemper 2008), prevailing climatic conditions, type of soil, content and quality of organic matter and other environmental factors (Tasho&Cho, 2016). With regard to compound physical-chemical properties, such as their molecular structure, size, shape, solubility and hydrophobicity, the sorption and fixation of these substances in soils differ considerably. Antibiotics can be either ionic, amphiphilic or amphoteric, and most of them are adsorbed easily and very fast (Kemper, 2008; Tasho&Cho, 2016).

The antibiotic classes more often detected in soil are macrolides (e.g. clarithromycin, roxithromycin, tylosin, dehydrato-erythromycin), sulphonamides (including the diaminopyrimidine trimethoprim), fluoroquinolones, and tetracyclines (Kemper, 2008; Kim et al., 2011; Burke et al., 2016). Leaching is restricted to a few antibiotics such as the sulfonamides (Jechalke et al., 2014; Tasho&Cho, 2016); hence, the largest fraction of most antibiotics applied to soils with manure is usually retained in the soil surface.

Nevertheless, while some compounds, e.g. β -Lactam antibiotics, are hydrolytically or biologically degraded within hours to a few days, depending on soil moisture, other compounds, such as tetracyclines or fluoroquinolones, may persist for several months to years (Jechalke et al., 2014). Indeed, it has been observed that tetracyclines not only occur in significant amounts in soil after fertilisation with liquid manure, but also persist and accumulate in the environment. This strong binding to soil-organic matter is based on the ability of the tetracyclines to form complexes with double-charged cations, such as calcium, which occur in high concentrations in soil (Kemper, 2008).

Besides their negative effects in terms of ecological impact, antibiotics could have an inhibitory effect on the anaerobic digestion process (Insam et al., 2015). For example, Alvarez et al. (2010) reported a reduction in methane production by >50% induced by oxytetracycline and chlortetracycline. Massé et al. (2014) conclude that anaerobic digestion is a quite efficient means of reducing antibiotic loads to soils, in particular at higher than ambient temperatures.

Widyasari-Mehta et al. (2016) investigated the behavior of doxycycline that is excreted by pigs mainly as unchanged active substance. Thus, doxycycline residues were found in liquid manures and digestates of biogas plants at concentrations of mg/kg dry weight. Therefore, first long-term storage simulation tests were performed at laboratory scale. Within the 170-d incubation periods under strictly anaerobic conditions, doxycycline was removed in liquid pig manure by 61% and in digestate by 76%. The calculated half-lives of 120 d and 91 d thus emphasized the persistence of doxycycline in both matrices. According to the high affinity of doxycycline to manure and digestate solids, however, the formation of non-extractable residues has to be taken into account as the predominant concentration determining process. Hence, these results confirmed that a full removal capacity for doxycycline cannot be reached through the long-term storage of farm fertilizers.

Methodologies:

For the extraction of most antibiotics from soil, the use of weakly acidic buffers in combination with organic solvents is recommended. Then, sample clean-up is generally performed by solid phase extraction (Thiele-Bruhn, 2003). For the determination of these pharmaceuticals in environmental matrices, especially when the simultaneous detection of compounds belonging to different classes is required, liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) is the technique of choice (see, for example: Ho et al., 2012; Jacobsen & Halling-Sørensen, 2006; Schlüsener et al., 2003; Ham-scher et al., 2002; Omar et al., 2016). In fact, when the analytes of interest are known and their authentic standards are available, mass spectrometry allows their unambiguous identification and quantification (target screening approach). However, the contaminants of interest might be metabolized by animals before excretion or transformed/degraded by microorganisms, etc. into the environment (see Wohde et al., 2016). In most cases, these metabolites/transformation products can be predicted; however, their authentic standards are rarely available. For this reason, high resolution mass spectrometry (i.e., by an instrumentation able to measure the accurate masses of unknown compounds with a mass error below 1-2 ppm, providing a list of the possible elemental compositions) could represent a valuable tool (see, for example, Sollic et al., 2016). This is known as suspect screening, which allows the tentative identification of the compounds of interest with the aid of dedicated software (for database search, fragmentation prediction tools, etc.). Therefore, high resolution mass spectrometry allows both the target screening of the selected chemical contaminants and the suspect screening of their predictable metabolites/residues, and will be used in chemical contaminants determination in both water and soil samples. For both soil samples (after a previous solvent extraction) and water samples, solid phase extraction using graphitized carbon black will be used for extraction/clean up followed by LC-MS/MS using low and high resolution instrumentations.

European legislation

Concentration limits of antibiotics in the environment are not regulated in EU, even though the growing concern has been taken into account with the prescription of environmental risk assessment of veterinary pharmaceuticals in and Europe (EEA, 2010).

European Environment Agency (EEA). 2010. Pharmaceuticals in the environment. Result of an EEA workshop, Technical report 1/2010. <http://www.eea.europa.eu/publications/pharmaceuticals-in-the-environment-result-of-an-eea-workshop>. Accessed 15 Jan 2017

• Estrogens

One of the main groups of endocrine disrupting compounds (EDCs) is constituted by natural hormones, synthetic hormones and their metabolites. Natural estrogenic steroid hormones are 17β - and 17α -estradiol (E2), estrone (E1), and estriol (E3), and they possess an estrogenic potency >100 times more potent compared to the exogenous EDCs (Hamid & Eskicioglu, 2012). However, also the synthetic estrogens 17α -ethynylestradiol (EE2), and diethylstilbestrol (DES) possess marked endocrine disrupting properties. EE2 is a derivative of the natural hormone E2, and is one of the most commonly used medications for humans as well as animals, since it is used to improve productivity by promoting growth, prevent and treat reproductive disorders in livestock (Aris et al., 2014). EE2 has become a widespread problem in the environment due to its high resistance to the degradation process and its tendency to (i) absorb organic matter, (ii) accumulate in sediment and (iii) concentrate in biota. Indeed, even though EE2 and E2 have a similar chemical structure, EE2 is a nonpolar and hydrophobic organic compound with low volatility and is more resistant to biodegradation (Aris et al., 2014).

The feminization of male fish due to estrogen contamination of water bodies has been reported for several countries worldwide (Aus Der Beek et al., 2016). Studies suggest that the estrogenic effects of E2 and E1 on fish species occur at concentrations of a few ng/L (Kjær et al., 2007), or even below 1 ng/L for EE2.

The primary estrogen contamination is suspected to originate from wastewater treatment plants; nevertheless, recent studies suggest that also land application of animal manure could be an important source of steroidal hormones for agricultural runoff (Dutta et al., 2012; Gall et al., 2015). Cattle excrete mostly E2 (α and β), E1, and respective sulfated and glucuronated conjugates, whereas swine and poultry excrete mostly α E2, E1, E3 and respective sulfated and glucuronated conjugates (Hanselman et al., 2003). The data on possible leaching of estrogens from manure-treated soil to water bodies are contradictory (Kjær et al., 2006) and incomplete (Kumar Khanal et al., 2006). Kjær et al. (2006) observed that when estrogen-containing manure is applied to and incorporated into the soil, conditions in the manure are likely to remain anoxic for quite some time, thereby retarding estrogen degradation. Solid-liquid separation of slurry, by removing organic dry matter, would have a greater impact on hormone levels than on pathogens because of greater hormone sorption to slurry organic matter (Amin et al., 2014; Amin et al., 2016). Mina et al. (2016) monitored estrogens in surface runoff after dairy manure application, and they detected E2 and E1 for up to 9 months after fall.

Aus der Beek and coworkers (aus der Beek et al., 2016), through a comprehensive literature review, collected the environmental concentrations for human and veterinary pharmaceutical substances reported worldwide in surface water, groundwater, tap/drinking water, manure, soil, and other environmental matrices in a comprehensive database.

In their survey, Dutta et al., (2012) stated that among the free forms of estrogens, only E1 was consistently detected in runoff samples, whereas sulfate species were the only conjugate species observed.

Whereas concentrations for the conjugated forms declined dramatically, concentrations for E1, although very low, persisted through the summer for surface runoff collected at the field edge.

The effect of anaerobic digestion on steroid hormones is controversial. It was observed that during digestion E3 could be transformed to E1, thus increasing the estrogenicity while decreasing estrogen concentration, because of higher estrogenic potency of E1 than E3 (Hamid & Eskicioglu, 2012). Under anaerobic conditions, both α - and β - E2 degrade predominantly to E1, but reversibly, and interconversion between isomers also occurs; furthermore, anaerobic biotransformation of α -E2 to E3 has also been observed (Gall et al., 2015).

Methodologies:

Fang et al. (Fang et al., 2016) wrote a review on analytical techniques for steroid estrogens in water samples, listing also reviews on the occurrence, fate and biodegradation of steroid estrogens in wastewater and manure, as well as on the elimination processes of E1, E2, E3, and EE2 from wastewater. For the determination of steroid hormones, gas chromatography or liquid chromatography (LC) coupled to tandem mass spectrometry (MS/MS) are used (Omar et al., 2016). However, when the simultaneous detection of free and conjugated forms is required, liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) is the technique of choice (see Tomšíková et al., 2012). In fact, when the analytes of interest are known and their authentic standards are available, mass spectrometry allows their unambiguous identification and quantification (target screening approach). Even if authentic standards for all the estrogens conjugated forms are not available, however, the main metabolites are known. Therefore, for both soil samples (after a previous solvent extraction) and water samples, solid phase extraction (SPE) using graphitized carbon black will be applied for extraction/clean up followed by LC-MS/MS using low resolution instrumentations. Only in case of ambiguity, also high resolution mass spectrometry will be employed. SPE followed by LC-MS/MS is also the indicative analytical method reported in the Decision EU 2015/495.

EU, Commission implementing Decision (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council.

Fang T. Y., Praveena S.M., deBurbure C., Aris A.Z., Ismail S.N.S., Rasdi I. 2016. Analytical techniques for steroid estrogens in water samples – A review. Chemosphere 165, 358-368

Ho Y.B., Zakaria M.P., Latif P.A., Saari N. 2012. Simultaneous determination of veterinary antibiotics and hormone in broiler manure, soil and manure compost by liquid chromatography-tandem mass spectrometry. J. Chromatogr. A 1262, 160-168.

Omar T.F.T., Ahmad A., Aris A.Z., Yusoff F.M. 2016. Endocrine disrupting compounds (EDCs) in environmental matrices: Review of analytical strategies for pharmaceuticals, estrogenic hormones, and alkylphenol compounds. TrAC Trend Anal. Chem. 85, 241–259.

Tomšíková H., Aufartová J., Solich P., Sosa-Ferrera Z., Santana-Rodríguez J.J., Nováková L. 2012. High-sensitivity analysis of female-steroid hormones in environmental samples. Trend Anal. Chem. 34, 35-58.

European legislation

There is any limit set at European level for steroid hormones in soil. The steroid hormones E1, E2, and EE2 are included in the watch list of substances for Union-wide monitoring as set out in Article 8b of Directive 2008/105/EC (Decision EU 2015/495).

EU, Commission implementing Decision (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council.

• PAHs/PCBs

Compost, digestate and biochar can have a positive effect on physical, chemical, and biological soil parameters due to their amending and/or fertilizers value. Organic pollutants are unwanted chemical compounds supplied through the feedstocks (wastes) or generated during the wastes management processes. However, little is known about the concentration, and transformation of persistent organic pollutants during biological and thermochemical processes that could further persist in the final products such as digestate, compost and biochar representing an environmental and human burden (Kusmierz and Oleszczuk, 2014).

Among them, PAHs (Polycyclic Aromatic Hydrocarbons) and PCBs (Polychlorinated biphenyls) should be monitored due to the negative impact that they could exert on human, living organisms and environment (Hale et al., 2012; Kusmierz and Oleszczuk, 2014; Govasmark et al., 2011). Especially workers employed in the handling of residual biomasses (i.e. digestate, compost, biochar) are particularly exposed. These contaminants could also affect the water quality through run-off and leaching process when such by-products are used as fertilizers and/or soil amenders. The final concentration of such organic contaminants will depend on the original feedstock and on the operational conditions of the wastes management processes used.

Similarly to heavy metals, PAHs and PCBs are reported to be lowly affected and degraded by anaerobic digestion and composting process (Brändli et al., 2007a). Heavy metals and organic pollutants (as PAHs and PCBs) may therefore be concentrated due to mass reduction during biogas production. Indeed, from the literature data, Brändli et al. (2005) concluded that, even if the median concentrations of the sum of 16 PAHs and 6 PCBs were higher in green waste (1803 and 15.6 µg/kg dm, respectively) than in organic household waste (635 and 14.6 µg/kg dm, respectively), nevertheless, compost from organic household waste and green waste contained similar amounts of Σ 16 PAHs and Σ 6 PCBs, (1915 and 39.8 µg/kg dm, and 1715 and 30.6 µg/kg dm, respectively). The concentrations of three-ring PAHs were reduced during the composting process, whereas five- to six-ring PAHs and Σ 6 PCBs increased by roughly a factor of two due to mass reduction during composting. Brändli et al., (2007a, 2007b) have monitored the PAHs and PCBs content during composting and anaerobic digestion of organic wastes. Concentrations of low molecular weight (LMW) PCBs increased during full-scale composting, whereas high molecular weight (HMW) congeners were slightly reduced. Further investigation on degradation mechanisms (including metabolites such as hydroxy-PCBs) could clarify the processes responsible for these alterations. Although increasing during composting, the total PCB input to agricultural land by compost application may be low, compared to other input pathways due to overall low PCB concentrations in this matrix (Brändli et al., 2007a). Indeed, sources of PCBs in compost and digestate are diffuse and aerial deposition is suggested to be the main input pathway (Brändli et al., 2007b). In contrast, PAH inputs to agricultural land by compost application can be considerable compared to other inputs (Brändli et al., 2007b). HMW PAHs remained stable during composting, whereas LMW compounds decreased (Brändli et al., 2007a). Thorough studies to identify sources of PAHs in compost are needed to lower PAH concentrations therein. The most realistic way of doing this seems to be a detailed investigation of input material at composting sites where PAH concentrations were high in repeated analyses, since indirect methods (characteristic PAH ratios, molecular markers, linear unmixing) did not reveal clear results. Digestion and press water need to be included in these evaluations since they were prone to even higher PAH concentrations (Brändli et al., 2007b). Beníšek et al. (2015) confirmed the range of PAHs previously reported in composts of different origin (27-21000 µg/kg, dm).

As in any combustion, pyrolysis also releases polycyclic aromatic hydrocarbons (PAHs) (Fagernäs et al., 2012). Their amount is dependent in particular on production conditions (Bucheli et al., 2015). Modern pyrolysis methods allow a significant reduction of the PAH pollution. High PAH levels are an indication of unsatisfactory or unsuitable production conditions. Hilber et al. (2011) have investigated the PAHs content (sum of 16 U.S EPA PAHs) in four different biochars of woods and agricultural residues. Values

ranging from 9.1 mg kg DM⁻¹ to 355 mg kg DM⁻¹ were reported according the pyrolysis temperature and feedstocks used. Hale et al. (2012) have investigated the PAHs content on various biochar produced form slow pyrolysis process and reported value ranging from 0.07 mg kg DM⁻¹ to 3.27 mg kg DM⁻¹. Interestingly, they reported that with increasing pyrolysis time and temperature, PAHs concentrations generally decreased. Concentrations of bioavailable PAHs in slow pyrolysis biochars ranged from 0.17 ng L⁻¹ to 10.0 ng L⁻¹ which is lower than concentrations reported for relatively clean urban sediments. Finally, Bucheli et al. (2015) have reported PAHs concentrations in biochar from 20 scientific publications. It is not discussed here, but PAHs have also been reported on bio-oil and syngas produced through the pyrolysis process (Bucheli et al., 2015). Finally, Kusmierz and Oleszcuk (2013) have highlighted that biochar production increases the PAHs content in surrounding soils and thus human risk. For this purpose, samples of soils collected in the immediate vicinity of traditional biochar pyrolysis producing plants were analyzed in PAHs content. The sum of the 16 PAHs varied within the range of 1.8 to 101 g kg⁻¹ for five different localities. In previous experiments, we showed that biochar has a high absorption affinity for PCBs and can significantly reduce the uptake of PCBs in plants (especially for di-, tri-, and tetrachlorobiphenyls) when added to soil (Wang et al. 2013; Fang et al. 2014).

Remark: Many literature sources have shown that biochar are effective in the immobilization of a wide range of organic and inorganic chemicals. Thus, it is conceivable that biochar application to soil could influence the plant uptake of a range of organic compounds thereby impacting plant growth, but this aspect has not received much attention in the literature so far (Wang et al., 2013).

Methodologies:

In digestate and compost, the analysis of PAHs and PCBs is realized using GC/MS-devices after a Soxhlet extracted with n-hexane for 8 h. A detailed protocol for the analysis of PAHs and PCBs is provided by Govasmark et al., 2011. On the contrary, it has been specified in in the EBC guidelines (2016) that most of the standard methods for testing PAHs are unsuitable for biochar due to the biochar's high adsorption properties. In that case, a soxhlet-extraction with toluol, analysed by GC-MS or HPLC is recommended. A detailed protocol for PAHs analysis in biochar has been reported by Hitler et al. (2012). The same protocol is recommended for the analysis of PCBs. In France, a protocol described through the **XP X33-012** Norm is generally used for the quantification PAHs and PCBs in compost and digestate.

European legislation

EU legislation with specific organic pollutant limit values for composts and digestates currently does not exist. In a broader context, Council Regulation (EC) No 1195/2006 of 18 July 2006 amending Annex IV to Regulation (EC) No 850/2004 (POPs Regulation) prescribes general maximum concentration limit values in waste for PCBs (50 mg/kg) and PCDD/F (15 µg/kg) (JRC, 2014).

In the End-of-waste criteria for biodegradable waste subjected to biological treatment (compost & digestate) technical proposals (JRC, 2014), a limit of 6 mg/kg dry matter is proposed for PAH16 (sum of naphthalene, acenaphtylene, acenaphtene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[ghi]perylene), in line with existing national legislation.

For **compost and digestate**, the French Norm NF-U-44051 recommend limit concentration for the following PAHs: fluoranthène, benzo(b)fluoranthène and benzo(a)pyrène. The annual flow limit on ten years are 6 g/ha/year, 4 g/ha/year and 2 g/ha/year respectively for fluoranthène, benzo(b)fluoranthène and benzo(a)pyrène. The limit values to not exceed are set up to 4; 2.5 and

1.5 mg kg⁻¹ MS respectively for fluoranthene, benzo(b)fluoranthene and benzo(a)pyrene. In the following Norm, no specific recommendations are made for PCBs.

As concerns for **biochar** used as soil amenders, no PAHs and PCBs thresholds are specified yet in the European soil protection regulations for soil conditioners and organic fertilizers. Nonetheless, different biochar certificate and / or quality protocol at been developed at the European and International level to test the biochar quality and standardize the product definition: Biochar Quality Mandate (BQM, 2013); European Biochar Certificate (EBC, 2012) and International Biochar Initiative (IBI, 2012). All these initiative have set threshold values for both PAHs and PCBs (Table 1). For instance PAHs thresholds of 12 mg kg⁻¹ and 300 mg kg⁻¹ have been reported respectively for EBC and IBI. PCBs thresholds.

BQM. Biochar Quality Mandate v. 1.0. 2013

IBI Standardized Product Definition and Product Testing Guidelines for Biochar That Is Used in Soil International Biochar Initiative - May 2012

EBC (2012) 'European Biochar Certificate - Guidelines for a Sustainable Production of Biochar.' European Biochar Foundation (EBC), Arbuz, Switzerland. <http://www.europeanbiochar.org/en/download>. Version 6.2E of 04th February 2016

Joint Research Centre (JRC), European Commission. 2014. End-of-waste criteria for biodegradable waste subjected to biological treatment (compost & digestate): Technical proposals, Final report, December 2013, Sevilla, Spain. doi:10.2791/6295

AFNOR: NF U44-051 Amendements organiques—Dénominations spécifications et marquage (2006).

• Polyphenols

Polyphenols content is an important parameter to be monitored during the agricultural wastes management processes. Polyphenols compounds are naturally present in several agricultural wastes streams such as winery and olive wastes industries (Cao et al., 2010; Da Porto et al., 2015; Monlau et al., 2014). Phenols can also be produced from biodegradation of naturally occurring aromatic polymers such as humic acids and tannins or from degradation of xenobiotic compounds such as pesticides (Fang et al., 2006). Some pre-treatments applied to increase biofuels production efficiency from lignocellulosic materials are also known to result in the production of phenolic compounds (*i.e.* vanillin, syringaldehyde, syringic acid...) (Monlau et al., 2014). Polyphenols levels are key indicators as they can affect the wastes management processes at different levels:

- By inhibiting most of bioprocess (anaerobic digestion, dark fermentation, bioethanol, succinic acid) involving microorganisms such as bacteria, strains or archaea (Alexandri et al., 2016; Monlau et al., 2014).
- Polyphenols if they are not degraded during bioprocess could also have detrimental effect on soil microorganisms or plant growth in the case of streams are used as soil amendment (Barbera et al., 2014; Levén et al., 2012; Monlau et al., 2014).

Polyphenols that are naturally present on some agricultural wastes (such as olive or grape industry wastes but also manure) or generated through pretreatment of lignocellulosic substrates have been identified as possible inhibitor of bioprocess (*i.e.* anaerobic digestion, dark fermentation, bioethanol, succinic acid). If the inhibition of the bioethanol fermentation process by phenols is well documented in literature, phenols have also been recently reported to inhibit other bioprocesses (Monlau et al., 2014). Generally, low molecular weight phenolic compounds are considered as more toxic compounds to micro-organisms than high molecular ones (Barakat et al., 2012). (Quéméneur et al., 2012) have investigated the inhibition of biohydrogen through dark fermentation process using mixed cultures in the presence of xylose (at 5g L⁻¹) and phenols (at 1g L⁻¹). A decrease of the hydrogen production of 23% was noticed in the presence of phenols. Similarly, (Alexandri et al., 2016) have investigated the succinic acid production from spent sulphite liquor (SSL), the by-product stream of the acidic sulphite pulping process,

rich in fermentable sugars and phenolic compounds. The removal of phenolic compounds from SSL led to higher succinic acid production (from 0.043 to 0.054 g_{succinic acid} g⁻¹ SSL) by both *Actinobacillus succinogenes* and *Basfia succiniciproductens* than in the case that untreated SSL was used (from 0.026 to 0.035 g_{succinic acid} g⁻¹ SSL). Then, the impact of polyphenols on the anaerobic digestion process have also been reported and concentration about 2g L⁻¹ have been reported to be inhibitory of the process (Chapleur et al., 2015; Poirier et al., 2016). In the case of a soil wastes stream application, organic contaminants such as polyphenols, if not sufficiently degraded in the bioprocess, can result in a digestate with a lower value as a fertilizer/amenders affecting both soil microorganisms (such as ammonia oxidizing bacteria) but also plant growth (Barbera et al., 2014; Levén et al., 2006; Levén et al., 2012) and groundwater quality through leaching and run-off. To avoid this detrimental impact on both bioprocesses and soil, several process could be applied before or after the bioprocess:

- An extraction of polyphenols through a pretreatment step (*i.e.* thermal, aerobic, thermos-alkaline...) or activated carbon adsorption could be recommended for the recovery of polyphenols as high value added molecules improving the profitability of the wastes management processes (Barbera et al., 2014; Gunay and Karadag, 2015; Serrano et al., 2017). However, few studies have studied until yet the economical aspect of recovering polyphenols before bioprocess (Serrano et al., 2017).
- Polyphenols are related to phytotoxic and antimicrobial effects, which makes conditioning treatments, such as composting, as an interesting option before the use of this waste as a soil fertilizers/amenders. Composting produced a degradation of the phytotoxic compounds, such as polyphenols, to give composts without a phytotoxic character (Bustamante et al., 2008).

Methodologies:

In the NoAW project, the **total polyphenols** content will be determined according the protocol of Folin-Ciocalteu (Singleton et al., 1999). Briefly, the reaction mixture contained 100 mL of extract or solvent, 500 mL of the Folin-Ciocalteu reagent, 1.5 mL of a sodium carbonate water solution (200 g/L), and 1.5 mL of pure water. After 2 h of reaction at ambient temperature, absorbance was read at 765 nm using a UV-Vis spectrophotometer. Gallic acid was employed as the standard. All analyses were performed in triplicate. Results were expressed as milligrams of equivalent gallic acid per 100 g of dried matter (mg GAE/100 g DM). The nature of the different polyphenols could be assessed by more sophisticated devices using the gas chromatography/mass spectrometry (GC-MS) or HPLC/UV detector or HPLC/ diode array detector.

Singleton VL, Orthofer R, Lamuela-Raventos RM. (1999) Analysis of total phenols and other oxidation substances by means of Folin-Ciocalteu reagent. *Methods Enzymol.* 299:152-178.

• Inert and Plastics

A range of diverse impurities can be present in original organic waste feedstock and thus remain in final by-products like compost, anaerobic digestion and biochar. There are sand, stones, glass, packaging materials and various pieces of metal, plastic, wood. These impurities cannot be always removed by source separation or by different barriers, sieves or traps through the processes. Absence of inerts, such as plastics or sharp particles, is a quality requirement both for sanitary issues (harmless contact through manipulation) or visual aspect of soil conditioners (Teglia et al., 2009). Indeed, the presence of any kind of impurities in products derived from organic waste has a negative impact on their quality and may constitute a health and environmental risk. Their use as fertilizer or soil conditioner could be accepted with difficulty by public and farmers (Aspray, 2016; Al Seadi and Lukehurst, 2012). However issues of inert materials mainly concern the characterization of organic solid wastes or the compost. For anaerobic digestion remaining physical impurities will result in problems in the process like equipment abrasion, accumulation and plant malfunctions (Jank et al., 2016). Practically little to no attention is

given for the presence of such contaminants in digestate or biochar. In UK, specification for digestate derived from source-segregated wastes includes limit values for man-made fragments and stones (PAS 110, 2010). From a statutory point of view, the determination of inert materials in the organic waste derived products and several countries established criteria and protocols for the compost. Variability in compost quality assessment end test methods have been recently discussed (Cesaro et al., 2015; Echarri-Bravo et al., 2017) suggesting the need to improve uniformity of standards.

Remark: it is important to note that this indicator does not take into account the particles size of inert which is a key factor of potential toxicity; especially when micro and nano scales are reached. Nanoparticles of plastics for example are able to penetrate physiological membranes and induce toxicity via accumulation and inflammatory process (Wright et al., 2013).

Methodologies:

The analytical method XP U 44-164 used to determine the inert fractions in by-products. It includes a bleach treatment to be able to easily distinguish the inert materials. This is performed after drying the material at 80°C in order to avoid plastic deterioration that can occur at higher temperature. After the destruction of non-synthetic organic matter a densitometric sorting procedure is performed with water and a calcium chloride concentrated solution.

- The raw sample (1kg), placed in a 2 mm mesh net, is subjected to 3 successive baths of bleach during at least 2 hours, 4 hours, and 12 hours respectively. Pieces of wood, pits, hard seeds which are not destroyed are put aside but not necessarily weighed.
- After rinsing the solid material > 2mm is placed in the water to separate the floating light elements (films and EPS plastics) and the sieved fraction > 5mm is gathered then dried and weighed.
- All remaining material is sieved at 2mm then dropped into a CaCl₂ solution (1,5kg/L). Floating elements (1<d<1.35) are sieved at 5 and 2 mm. Obvious non plastic material (pieces of wood, pits...) is removed. Thus, we catch the > 5mm and 2-5mm other plastics fractions which are well rinsed, dried and weighed.
- The sinking heavy part (d>1.35) is well rinsed then dried before transfer onto 2 and 5 mm. For each sieved fractions, glass, metal and stone/calcareous particles are manually sorted then weighed.
- Finally we get the masses for components of interest:

Even if it is not required in the norm, TS and VS could be determined for the sample and all fractions (including < 2mm) in order to ensure the final mass balance.

AFNOR NF U44-164 (2004) Amendements organiques et supports de culture - Méthode d'analyse des composants inertes - Méthode à l'eau de Javel. French norm for organic soil improvers - Method in the bleach.

European legislation

European legislation has set some threshold values for the inerts in compost and digestate that depend of each country's legislation. For instance, in France, to be sold as a product, compost must fulfill criteria of the standard NF U44-051 as plastic film + expanded polystyrene (EPS) > 5 mm (< 0.3 % DM); other plastics > 5 mm (< 0.8 % DM); Glass + Metal > 2 mm (< 2 % DM). In the publication of Teglia et al. (2011) a table with different European National Guidelines for impurities in organic residues has been provided.

AFNOR: NF U44-051 Amendements organiques—Dénominations spécifications et marquage (2006).
 Teglia, C., Tremier, A., Martel, J.L., 2010. Characterization of Solid Digestates: Part 1, Review of Existing Indicators to Assess Solid Digestates Agricultural Use. Waste and Biomass Valorization 2, 43-58.

• **Soil and plant indicators**

Besides, to define indicators for soil, it is also important to take into account the modification implied by wastes management processes on further plant growth. Indeed, the re-use of by-products (*i.e.* biochar, digestate, compost...) can further affect the plant growth and development. If soil indicators are useful to assess the fertilizers, amending and innocuity parameters of soil that can affect plant growth, they can be limited in predicting the real impact on plant growth. For these purpose, three tests will be carried out during the project to assess the interaction soil/plant: seed germination tests, leaf growth test and root growth tests (Table 4).

Table 4. Soil/plants indicators recommended to assess for the environmental sustainability evaluation of the wastes management processes developed.

Indicators names	Description	Units or Parameters quantified
Seed germination	Estimate the risk of inhibition of seed germination in contact with different concentrations of tested products	Germination index (%)
Leaf growth tests	Evaluate the risks of inhibition of the aerial plant growth parts brought in contact with the products	TS and VS of the aerial parts (g TS or g VS)
Root growth tests	Evaluate the risks of inhibition of the roots plant growth parts brought in contact with the products	Length of the longer roots and TS the root parts (g TS or g VS)

The current shift towards bioenergy and value added molecules production increases streams rest products (Albuquerque, 2012; Gell et al., 2011). Among them digestate and/or compost from anaerobic and aerobic processes; biochar from thermochemical processes like pyrolysis but also end of life products like bioplastics that can be used to soil application or return to soil for biodegradation (Monlau et al., 2016; Nkoa, 2013). Nonetheless, besides to have a high nutrients value, such by-products could also be composed of residual inhibitory compounds (salt, ammonium, water extractable Zn and Cu, VFAs, polyphenols...) that can cause unfavorable impacts on the soils plant system like prevention or delay of seed germination, plant death or marked reduction in growth (Albuquerque, 2012). If the chemical and biochemical properties can give some useful information on the agronomic properties, plant bioassays are highly recommended in parallel to evaluate the benefit of these wastes streams on plant growth. Plant bioassays are simple, reproducible and rapid tests to assess the phytotoxicity and efficiency of these residual by-products. Phytotoxicity tests have been established as general academic and regulatory tests for chemical and environmental toxicity (OECD, 2006). Plant tests generally applied can be divided into three main categories: germination tests (including root assessments), growth tests (assessment of top growth and sometimes root mass), combinations of germination and growth (Cesaro et al., 2015). Typically, the germination test indicates whether a biomass may cause toxicity in the early stages of plant growth (short term maturity tests) whereas vegetative tests (seedling tests) are able to supply information about the agronomic value of the products (long term maturity test) (Tambone et al., 2015), with different conclusions depending on the time of assessment. The GI test is generally performed on cress, ray grass seeds and lettuce (Albuquerque, 2012; Teglia et al., 2010). Currently, innocuousness thresholds for the germination index vary from 50 to 80% according to authors and wastes

(Teglia et al., 2010). Plant growth tests could be realized on various plants such as lettuce, wheat and radish (Gell et al., 2011; Tambone et al., 2015).

Few studies have investigated in the literature the used of plant bioassays to assay the efficiency and possible phytotoxicity effects that could be bring by the wastes management streams processes when there are used in agronomic purpose (Alburquerque, 2012; Gell et al., 2011; Tambone et al., 2015).

First of all, several studies have investigated the effect of compost addition on GI and plant growth (Tambone et al., 2015). For instance, Selim et al. (2012) have investigated the phytotoxicity of agricultural composts (i.e. made up of corn stalks, cotton stalks and bagasse in mixture with manure, mature compost or sewage sludge) using the Germination Index (GI) during compost period. A negative correlation was observed between the GI of cress with NH_4^+ , Cu and Zn content, while positive correlation was observed with NO_3^- , P and K content (Selim et al., 2012). Tambone et al. (2015) have investigated the GI and plant growth test on compost originating from the solid fraction of digestate derived from pig slurry (Tambone et al., 2015). They investigated plant bioassays on five compost from solid fraction (SF) of agricultural digestates. A lignocellulosic bulking agent (BA) was used in the proportion of SF: BA ratio of 4:1 on a fresh weigh basis. Interestingly, all composts did not exhibit any germination inhibition with GI (%) varying from 63% to 109 % of the control samples (Tambone et al., 2015). Then plant growth assays were realized at different doses of compost (from 15 to 145 Mg DM ha^{-1}) and the average plant production was similar or higher than that of the control suggesting not adverse effect on plant growth.

GI (%) and plant growth bioassays have also been realized on digestate from agricultural wastes (Alburquerque, 2012; Gell et al., 2011). For instance, Alburquerque et al. (2012) have tested various supernatants of anaerobic digestate in bioassays involving seed germination and seedling growth. Among the 12 digestates examined, at a concentration of 1%, most of the digestates exceeded the threshold value for GI, in both the cress and lettuce bioassays; thus these digestates could be considered to have plant nutrient or plant growth stimulant. Nonetheless, at higher concentration of digestate the GI decrease for quite all digestate. Alburquerque et al. (2012) recommended that in order to avoid phytotoxicity, digestate application to soil should be done well in advance of sowing, avoiding direct contact with young plants or germinating seed. Gell et al. (2011) have also investigated the impact of anaerobic digestate (from cow manure and pig slurry) on plant growth (i.e. wheat, radish, lettuce) performances cultivated on a sandy soil. Digestate were added at a concentration of 50 mg total N kg^{-1} dry corresponding to 150 kg N ha^{-1} . For the two digestates investigated, none of the digestates were significantly different from the control interm of plant accumulation (shoots and roots) (Gell et al., 2011).

The effect of biochar on GI and plant growth have been reported to have negative impact (Kookana et al., 2011) but also positive impact (Keller et al., 2008; Opatokum et al., 2017). These differences can be explained by the feedstock used but also by the pyrolysis operational conditions that will directly influenced the physico-chemical properties of the biochar produced. In general rules, it seems that an increase of the pyrolysis process, results in biochar will less inhibitory compounds (Opatokun et al., 2017). Opatokum et al., (2017) have investigated the GI of various biochars produced from anaerobic digestate. Interestingly, they reported that anaerobic digestate have a toxicity effect with the smallest seed germination index (GI) of 48.1% In parallel, all biochars indicated GI above 105% illustrating a decrease in phytotoxic precursors and also reflect gradual degradation of feedstock's primary and secondary intermediate compounds (i.e. phenolic, polyalcohols and volatile fatty acids) as charring temperature changes. Similarly, sorghum based biochar was reported to increase germination and seedling growth despite being enriched with tar produced through fast pyrolysis (Keller et al., 2008). Finally, Gell et al. (2011) have investigated the impact of eight biochars produced from various biomasses (from bamboo, manure and manure digestate) and different pyrolysis temperature on the plant growth (i.e. wheat, radish, lettuce) performances on a sandy soil. Interestingly, biochars addition ranged from beneficial to detrimental effect depending on the original feedstock and temperature of pyrolysis (Gell et al., 2011).

As for bioplastics, the NF EN 13432 Norm for bioplastics have also defined a seed germination test to evaluate the potential toxicity of compost in which bioplastics have been disintegrated. The protocol applied is adapted from the OECD (2006) protocol. It is recommended that the germination rate and plant biomass of the sample composts be greater than 90% of those of the corresponding control compost.

Methodologies:

Phytotoxicity tests have been established as general academic and regulatory tests for chemical and environmental toxicity (OECD, 2006). In the case of the NoAW project, the Germination Index will be determined according an adapted protocol from the French Norm “XP U 44-165”.

The germination Index is defined according the following equation:

$$GI (\%) = \frac{\text{Number of seed germination in the soil + products}}{\text{Number of seed germination in the soil control}} * 100$$

Plant growth bioassays will be determined through an adapted protocol from the French Norm “XP U44-167”. The germination Index and the aerial biomass accumulation (mg fresh matter or dry matter per pot) are generally used as indicators for plant growth bioassays. In some cases, the total biomass accumulation (shoots + roots) can be considered. Generally, the efficiency of the exogenous organic matter is compared with respect to three types of control: unfertilized soils and mineral fertilizers.

As for bioplastics, the NF EN 13432 Norm for bioplastics have also defined a seed germination tests to evaluate the potential toxicity of compost in which bioplastics have been disintegrated. The protocol applied is adapted from the OECD (2006) protocol. It is recommended that the germination rate and plant biomass of the sample composts be greater than 90% of those of the corresponding control com-post.

XP U 44-165. Test rapide d'évaluation de la maturité d'un compost et de caractérisation des matières premières vis-à-vis de la germination du cresson, février 2004.

XP U44-167. Essai d'évaluation de l'émergence et de la croissance de plantes supérieures dans les conditions d'utilisation des amendements organiques, Juillet 2005.

EN13432 Requirements for packaging recoverable through composting and biodegradation (2000).

OECD guidelines for the testing of chemicals, in: Test No. 208: Terrestrial Plant Test. Seedling Emergence and Seedling Growth Test, OECD Press, Paris, 2006.

4.3.2 Air indicators

The wastes management processes that will be developed under the NoAW project can also affect the air quality through air emissions (GHGs and airborne pollutants). For this purpose, several indicators for the air item will be carried out (Table 5).

The air emissions are mainly coming from the following sources:

- Harvest and transport of biomass from the field to the wastes management plant.
- Storage of biomass in uncovered tank (*i.e.* manure, animal slurries digestate, compost).
- Wastes management processes (GHGs emissions but also pollutants emissions). GHGs emissions saved by renewable products and reduction of mineral fertilizers

- Soil emissions or carbon storage through carbon mineralization but also ammonia and nitrous oxide emissions due to wastes streams return.

Table 5. Air indicators that are recommended to be addressed.

Types of indicators	Indicators names	Description	Parameters quantified
Indicators of Climate changes	Greenhouse Gases emissions (GHGs)	Determination of the GHGs emissions that contribute to climate change and associated with the wastes management processes: Carbon dioxide (CO ₂); Methane (CH ₄); Nitrous oxide (N ₂ O); etc.	kg CO ₂ eq kWh ⁻¹ or kg ⁻¹ end-product
	Sinks and sequestration of CO ₂	Determination of the GHGs emissions saved by the wastes management processes, but also due to the by-products (digestate/compost/biochar) return to soil that contribute to create CO ₂ sequestration especially in the case of biochar.	kg CO ₂ eq / ha. year
Airborne pollutants from by-products handling and spreading	Ammonia (NH ₃ emissions)	Determination of ammonia emissions during the handling of by-products especially digestate	m ³ / kg by-products
	Bioaerosols (in composting process)	Determine the total or specific aerosols produce through composting process: microorganisms (bacteria, fungi, virus, protozoa, algae, pollen. . .) as well as biomolecules (toxins, debris from membranes. . .)	UFC, gene copies, or cells m ⁻³
Airborne pollutants from process	Airborne emissions from process NO _x , CO, VOC, SO ₂	Evaluate the emissions of airborne pollutant during processes (<i>i.e</i> distillation process of bio-ethanol or biofuels combustion for instance)	ppm
	Particulate matter (PM 10)	PM10 measures mass per unit volume of all airborne particles less than 10 μm diameter and thus includes those particles measured by PM2.5.	μg m ⁻³

➤ **Greenhouse Gases emissions (GHGs)**

Estimated net carbon equivalent (Ceq) flux to the atmosphere is recommended to measure the effect of bioenergy systems on atmospheric concentration of greenhouse gases that contribute to climate change (IPCC, 2007). To estimate net Ceq flux associated with bioenergy, we recommend that nitrous oxide (N₂O) flux and carbon dioxide (CO₂) flux be considered. N₂O is emitted directly from soil during both nitrification and denitrification (Bouwman et al., 2010), as well as indirectly when volatilized nitric oxide and nitrogen dioxide (NO_x) and ammonia (NH₃) are deposited offsite and converted to N₂O or when leached nitrate is denitrified in waterways (Adler et al., 2007). N₂O global warming potential is 310 times higher than that of carbon dioxide (Börjesson and Berglund 2007). Soils in general contribute more than half of the world's emission, and agricultural soils in particular account for about half of total soils emissions (Denman et al. 2007).

In addition to CO₂ and N₂O, methane (CH₄) can be important in calculating Ceq emissions (McBride et al., 2011). Briefly, CO₂ emissions are emitted during the use of fossil energies but also during the use

of industrial fertilizers in agriculture but also the mineralization of the organic matter returned back to the soil. The methane (CH₄) emissions can be emitted during organic product storage (in uncovered tank) and spreading (Gioelli et al., 2011; Balsari et al., 2013) but also from biogas plant leaks (generally less than 1% of biogas produced, Fantin et al., 2015). Finally, the spreading of organic residues in soil can also be responsible for nitrous oxide emissions (Nkoa, 2014). Estimated values for these various sources (i.e. N₂O, CH₄ and CO₂) can be collected and summed using the life cycle assessment (LCA) approach.

➤ Sinks and sequestration of CO₂ (GHGs)

The carbon sink and sequestration has attracted a lot of attention these last decades as a possibility to mitigate GHGs emissions and climate changes. The soil return of by-products (*i.e.* biochar, digestate, compost) is directly linked to the carbon sequestration. Indeed soil application of exogenous organic matter (Lashermes et al., 2009) could both contribute to the environmental issue of improving C sinks to mitigate CO₂ and to the restoration of soil properties. As previously mentioned in the amending part, the C mineralization will depend on the soil typology, climate but also nature of the organic matter applied. Generally the C mineralization is decreasing in the following order feedstock > digestate > compost > biochar. These results of C mineralization are depending on the nature of the carbon and soil amenders can be classified in three categories:

- Digestate with **still labile and partially stabilized** carbon (Monlau et al., 2016; Albuquerque et al., 2011). Indeed, the complete exhaustion of the most labile organic fraction during the anaerobic process, in order to obtain digestates with a high stability degree, is not easy to achieve at the industrial level, the main objective of the anaerobic co-digestion being the production (Albuquerque et al., 202).
- Compost **with stable** carbon. Composting is the aerobic degradation of organic matter and gives to a stable organic matter and is generally applied on solid anaerobic digestate to improve its stability (Bustamante et al., 2012). Hartz et al. (2000) have investigated the C mineralization of various manure samples. It was shown that C mineralization of manures averaged 35 % of the initial C content in 24 weeks whereas C mineralization of compost averaged only 14%.
- Biochar with **recalcitrant** carbon. Biochar has potential to sequester carbon in soils and simultaneously improve soil quality and plant growth (Monlau et al., 2015).

For instance, Socrates Schouten et al. (2011) have investigated the carbon emissions of three by-products (cattle manure, from which anaerobic digestate was obtained, which was subsequently pyrolysed) on a sandy soil in a laboratory incubation study. The highest losses of soil C from biological activity (CO₂ respiration) were observed in manure treatments (39% and 32% for loess and sandy soil), followed by digestate (31% and 18%), and biochar (15% and 7%).

Another important consideration is the incorporation of biochar in soil management which has been proved to improve soil properties but also reduce potential emissions like nitrous oxide (Martin et al., 2015). Nonetheless, such studies are still in their infancy and further research especially in long term field experiments are required to validate these previous observations. Finally, Cayuela et al. (2010) recommend that GHG (emissions and sinks) dynamics of by-products after soil amendment cannot be ignored and should be part of the lifecycle analysis of the various bioenergy production chains

Methodologies:

In the case of the NoAW project, the greenhouse gases emissions will be determined using Life Cycle Analysis philosophy with recognised methods (ex : IPCC 2007 via RECIPE). Depending on the chosen perimeter, the results can be compared between different waste reuse ways sectioned in the NoAW project and the literature.

IPCC, 2007. In: Core Writing Team, Pachauri, R.K., Reisinger, A. (Eds.), *Climate Change 2007: Synthesis Report. Contribution of Working Groups I, II and III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*. IPCC, Geneva, Switzerland, http://www.ipcc.ch/publications_and_data/publications_ipcc_fourth_assessment_report_synthesis_report.htm(accessed January 2011).

Note 3: The indicators of GHGs emissions and carbon sinks are closely related to Life Cycle Assessment (LCA) and for this purpose more explanation on identification/characterization and methodologies will be provided in the **WP2**.

Airborne pollutants are important to assess as they can be responsible for environmental damage but also have detrimental impact on the human health.

➤ **PM 10 and PM2.5**

PM10 and PM2.5 are also important indicators to be addressed (McBride et al., 2011). PM10 measures mass per unit volume of all airborne particles less than 10 μm in diameter and thus includes those particles measured by PM 2.5. In addition to fine particles, PM10 includes coarse particles, those between 2.5 μm and 10 μm in diameter. Agricultural systems can affect this coarse fraction through tilling and solid biomass combustion (Aneja et al., 2009, McBride et al., 2011). PM2.5 measures mass per unit volume of all airborne particles less than 2.5 μm in diameter, also known as the fine particle fraction (McBride et al., 2011). Bioenergy systems can contribute to fine particulate pollution (PM2.5, PM10) through different ways as solid biomass combustion or through the emission of various secondary particulate during biofuels or fossil fuels combustion, handling and spreading of feedstocks and by-products, but also soil emissions (McBride et al., 2011). Fine particles are generally classified as “primary” (soot, dust...) directly emitted from the point source but also secondary emitted to the atmosphere from gaseous emissions (*i.e.* ammonium, organic aerosols). A specific focus will be made on the ammonium emissions and bioaerosols.

• **Ammonium**

Ammonia emissions occurred mainly during the storage of anaerobic digestate in uncovered tank but also during its spreading on field (Balsari et al., 2013). Ammonia emission from anaerobic digestates is affected by management and environmental factors such as storage conditions, methods of application, concentrations of ammonia in the digestate, pH, temperature, air velocity, surface area and moisture (Sommer and Hutchings 2001; Sandars et al. 2003; Holm-Nielsen et al. 2009). Atmospheric NH_3 can further impact the environment through particulate matter formation through particulate matter formation, aquatic eutrophication and soil acidification (Balsari et al., 2013). For instance, Gioelli et al. (2009) found average daily NH_3 emission rates from stored non-separated digestate ranged between 2.06 and 4.44 gNH_3 per m^2 surface and between 7.89 and 14.6 gNH_3 per m^2 surface from digested liquid fraction. Gericke (2009) have evaluated the NH_3 emissions after anaerobic digestates application between 7 and 24 % of applied $\text{NH}_4\text{-N}$ as opposed to 3 to 8 % for animal slurries. Wulf et al. (2002) have investigated the emission of NH_3 of an anaerobic digestate using four spreading application technique. This anaerobic digestate was produced through combined anaerobic fermentation of 70% dairy cow slurry together with 30% organic household waste (per weight). Interestingly, Wulf et al. (2002) quantified these emissions at about 350, 275, 160 and 50 $\text{mg NH}_3\text{-N m}^{-2} \text{h}^{-1}$ within the first 10 h following application of liquid digestate through splash plate, trailing shoe, harrow and injection methods, respectively. In composts process, under the action of bacteria, organic nitrogen is mineralised within the biofilm, as, for the most part, the ammonium ion (NH_4^+) adding to mineral nitrogen content already present at the beginning of composting. Some of this nitrogen is volatilized as ammonia (NH_3) (ADEME, 2012).

Methodologies:

Airborne ammonia can be determined by monitoring sulfuric acid impregnated carbon bead tubes (USA department of Health and Human services, 1992).

USA department of Health and Human services: Occupational safety and health guideline for ammonia (1992).

• **Bioaerosols**

Composting is a method of waste management based on the biological degradation and stabilization of organic matter under aerobic conditions resulting in a sanitized and stabilized product rich in humic substances “called compost” that can be used as soil amenders and/or fertilizers. Some composting process activities especially during open windrow composting result in the release of micro-organisms into the atmosphere called “bioaerosols”. The implications of the release of bioaerosols is especially significant for composting plants operating in the open because their bioaerosols are released directly into the surrounding environment without any pretreatment using biofilters or bioscrubbers (Wery et al., 2014). Bioaerosol release from composting plants is a cause of concern because of the potential health impacts on site workers and local residents (Sanchez-Monedero et al., 2005). The term “bioaerosol” encompasses all particles having a biological source that are in suspension in the air and includes microorganisms (bacteria, fungi, virus, protozoa, algae, pollen. . .) as well as biomolecules (toxins, debris from membranes. . .) (Sykes et al., 2011). Bioaerosols are mainly released during processes that involve vigorous movement of material, mainly during fresh waste delivery, shredding, compost pile turning, and compost screening (Sanchez-Monedero et al., 2005; Wery et al., 2014). For instance, Sanchez-Monedero et al., (2005) have monitored the amount of *A. fumigatus* and total *mesophilic bacteria* generated at a typical green waste composting plant over 1 year of normal operation. The background levels for *A. fumigatus* and mesophilic bacteria varied within the range from $<10^2$ up to 10^3 cfu m^{-3} . The concentrations measured at locations downwind, potentially considered as sensible receptors, when no vigorous activity was taking place were no different from the background levels. Vigorous activities such as shredding, turning, and screening were identified as the major sources of bioaerosol generation and release and caused increases in both *A. fumigatus* and mesophilic bacteria concentrations on the adjacent footpath up to 2 log units higher than background levels (Sanchez-Monedero et al., 2005).

Note 3: H_2S production in biogas due to the anaerobic digestion of rich sulfur substrates need also to be considered. The distillation process of bioethanol but also combustion of biofuels (syngas, biogas...) can also be responsible for the emissions of potential contaminants such as CO, NO_x , CO, VOC, SO_2 . Chevalier et al. (2005) have evaluated that the cogeneration of 207 g CO_2/Nm^3 , 400 mg $NO_x/N m^3$, 500 mg $CO/N m^3$, 400 mg $VOC/N m^3$, 9.4 mg $SO_2/N m^3$.

Methodologies:

• Even if bioaerosols content will not be directly measured during the NoAW Framework, several Norm exist for the quantification of bioaerosols.

Among them:

The EN13098: 2000 Workplace Atmosphere - Guidelines For Measurement Of Airborne Micro-organisms And Endotoxin;

The EN14031:2003 Workplace atmospheres. Determination of airborne endotoxins;

The EN 14042: 2003 Workplace atmospheres. Guide for the application and use of procedures for the assessment of exposure to chemical and biological agents;

The EN 14583: 2001 Workplace atmospheres. Volumetric bioaerosol sampling devices. Requirements and test methods.

4.3.3 Water indicators

Using organic residues for land application can also result in environmental negative impact by ground-water pollution by leaching and run-off of both nutrients and chemical contaminants. Water indicators are important sustainability indicators to be monitored during agricultural wastes management processes. Indeed, the wastes management processes can also lead to surface and groundwater pollution and several indicators should be monitored. Such pollution can occur during the leaching of wastes handling but also during run-off and leaching after spreading of by-product like digestate and compost. Water indicators are affected by some of the same pressures that influence soil indicators (e.g., fertilizer application and vegetative cover). In contrast to soil indicators, water indicators can change more rapidly and integrate changes over an entire watershed, thereby allowing for finer temporal resolution and broader spatial integration of relevant effects (McBride et al., 2011).

Table 6. Water indicators that are recommended to be assessed.

Indicators names	Description	Units
Water consumption	Define the quantity of water used during the wastes management processes	m ³ kWh produced or kg interest product
Water quality	Biochemical Oxygen Demand (5 days BOD); Nutrients load P-form: PO ₄ ³⁻ ; N-form: nitrate, nitrite, ammonium.	g or mg / L water
Pathogens	Determination of pathogens released from soil to water	CFU / L water
Heavy metals (As, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Se, Zn)	Determination of the main trace elements that could have a negative impact on the soil and micro-organisms	mg or ng / L water
Pharmaceuticals (e.g. veterinary drugs)	Determination of veterinary antibiotics and their metabolites	mg or ng / L water
Pesticides	Determination of pesticides	mg or ng / L water
Estrogenic compounds	Determination of natural and conjugated estrogens	mg or ng / L water
Organic trace compounds	Determination of Polycyclic Aromatic Hydrocarbons (PAHs) Polychlorinated biphenyls (PCBs)	mg or ng / L water

➤ Water quality and quantity

Among them the **quantity of water** (L / kg or m³ of end-products) are important to be considered especially during the Life Cycle Assessment analysis. Most consumptive water use in biorefineries consists of evaporation from cooling towers and dryers/evaporators during distillation (NRC, 2008). Total water withdrawal is typically metered and easily reported by biorefinery managers. Quantity of water used for irrigation in the case of dedicated crops for bioenergies purpose should also be included.

➤ **5-day BOD**

The so-called **5-day BOD** measures the amount of oxygen consumed by biochemical oxidation of waste contaminants in a 5-day period. The total amount of oxygen consumed when the biochemical reaction is allowed to proceed to completion is called the Ultimate BOD. The Ultimate BOD is too time consuming, so the 5-day BOD has almost universally been adopted as a measure of relative pollution effect.

➤ **N and P compounds**

Water quality can be damaged by excess of P and nitrogen (N, found in ammonia, nitrite, nitrate) which are two important parameters to be monitored. Concentrations of nitrate and total phosphorus (P) in streams are indicators of potential eutrophication. Whereas aquatic systems respond to nitrogen (N) in other forms, nitrate is usually the most abundant form.

Nitrate from the fertilizer (digestate, compost...) not taken up by crops in fields and grass in lawns can enter water bodies in runoff.

Phosphorus (P), like nitrogen (N, found in ammonia, nitrite, nitrate), is an important nutrient for plants and algae. Because phosphorus is in short supply in most fresh waters, even a modest increase in phosphorus can cause excessive growth of plants and algae that deplete dissolved oxygen (DO) as they decompose. Phosphorus is present in waste waters in inorganic and organic forms. The inorganic forms are orthophosphates (*i.e.* $\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$) and polyphosphates and it is the predominant form. Phosphorus discharge has to be controlled in the same way as nitrogen discharge in order to avoid eutrophication of surface waters. It was reported that, to avoid algal blooms under summer conditions, the critical level of inorganic phosphorus is near 0.005 mg/L (JRC, 2017).

Methodologies:

Sediment is usually measured as a concentration of total suspended solids (TSS), which is the dry weight after filtering a water sample, expressed in mg per liter. To determine a suspended sediment load (mass/time), the TSS concentration must be multiplied by the flow rate (volume/time).

The laboratory test procedures for determining the above oxygen demands are detailed in the following sections of the "Standard Methods for the Examination of Water and Wastewater" available at www.standardmethods.org

As in the NoAW project, the water quality indicators will not be directly assessed, few information have been provided and the most important indicators cited. Nonetheless, more information on water indicators can be found in the report of the JRC (2017).

JRC (2017): Best Available Techniques (BAT) Reference Document for Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector

• **Waterborne pollutants**

The wastes management processes will also be responsible for waterborne pollutant emissions that should be addressed. Among them, potential run-off and leaching of pathogens and chemical pollutants present in soil. Indeed the soil return of some by-products (*i.e.* digestate, compost, biochar...) can be responsible of water contamination.

➤ Pathogens

Water quality in terms of bacterial pathogens is assessed by not analyzing each possible pathogenic organism, which may enter the water from the soil, air or other sources because that would be a tremendous work, especially as many pathogens are difficult to cultivate or even uncultivable. Therefore, one has agreed to focus the search of possible pathogenic bacteria via the analysis of indicator bacteria, which are comparably easy and cheap to analyze, so that they can be analyzed in most water laboratories throughout the world (Ramirez-Castillo et al., 2015; Saxena et al., 2015). Culture-dependent methods are preferred for indicator bacteria, as those result in CFU / 100 ml, which can best be compared with threshold limits. Bacterial pathogens and indicators relevant for quality of groundwater and surface water differ not much from the drinking water parameters, so that the logic parameters sum up to *E. coli* and coliform or fecal coliform bacteria as indicators for fecal pollution, plus gram-positive enterococci as those bacteria might survive longer in water than gram-negative indicators. Furthermore, *Clostridium perfringens* spores complete the bacterial parameters.

Methodologies:

Methodologies how to analyze the different bacterial indicators are given in the European Drinking Water directive 98/83/EC. Threshold limits for each pathogen or indicator are given as CFU per 100 ml water: *E. coli*, coliform, Enterococci, *Clostridium perfringens* spores: 0 / 100 ml water.

Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption.

➤ Chemical contaminants

The following contaminants that have been previously defined for soil indicators should be addressed also to determine the potential contaminants in water. Indeed, during the application of by-products (*i.e.* biochar, digestate, compost) in the agricultural sector can lead to potential run-off and leaching of organic contaminants and heavy metals. This case is especially true for digestate and to a lesser extent to compost. For biochar is not really clear yet and some studies have shown that biochar can significantly reduce the leaching of contaminants and nutrients (Inyang et al., 2012; Ioannidou et al., 2007).

Methodologies:

Chemical contaminants in water will be determined with the same methodologies used in soil. For pesticides extraction, see for example, Di Corcia et al. (2000). Generally, water samples will be directly extracted by solid phase extraction (SPE) using graphitized carbon black as adsorbent material, followed by LC-MS/MS analysis. SPE/LC-MS/MS is also the indicative analytical method reported in the Decision (EU) 2015/495 in the watch list for some substances (the relative maximum acceptable method detection limit in ng/L is also reported: EE2 (0.035 ng/L); E2, E1 (0.4 0.035 ng/L); macrolide antibiotics (90 ng/L); methiocarb (10 ng/L); neonicotinoids (9 ng/L).

Commission implementing Decision (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council.

Di Corcia A., Nazzari M., Rao R., Samperi R., Sebastiani E. 2000. Simultaneous determination of acidic and non-acidic pesticides in natural waters by liquid chromatography–mass spectrometry. J. Chromatogr. A, 878, 87–98.

European Legislation

In the Directive 2008/105/EC, the Commission establishes environmental quality standards (EQS) so as to limit the concentrations of certain chemical substances that pose a significant risk to the environment or to human health in surface waters in the European Union (EU). These standards are complemented by a requirement to establish inventories of the discharges, emissions and losses of these substances in order to ascertain whether the goals of reducing or eliminating such pollution have been achieved. The list of priority substances (Dir. 2008/105/EC) includes 45 substances (many pesticides), and for 27 of them is indicated a maximum allowable concentration (MAC) in surface water:

Pesticides - alachlor: 0.7 µg/L; atrazine 2 µg/L; chlorfenvinphos 0.3 µg/L; chlorpyrifos 0.1 µg/L; diuron: 1.8 µg/L; endosulfan: 0.01 µg/L; isoproturon: 1 µg/L; simazine: 4 µg/L; quinoxifen: 0.54-2.7 µg/L; aclonifen: 0.012-0.12 µg/L; bifenox: 0.04-0.4 µg/L; cybutryne: 0.016 µg/L; cypermethrin: 0.06-0.6 ng/L; dichlorvos: 0.07-0.7 ng/L.

PAHs – anthracene: 0.6 µg/L; fluoranthene: 0.12 µg/L; naphthalene: 130 µg/L; benzo[a]pyrene: 0.027-0.27 µg/L; benzo[b]fluoranthene and benzo[k]fluoranthene: 0.017 µg/L; benzo[ghi]perylene: 0.82-8.2 ng/L.

Heavy metals – Cd and its compounds: 0.45-1.5 µg/L; Pb and its compounds: 14 µg/L; Hg and its compounds: 0.07 µg/L; Ni and its compounds: 34 µg/L.

In the watch list of substances to monitor in water (Dec. EU/2015/495 pursuant to Dir. 2008/105/EC) are included 10 substances or class of substances, including the estrogens EE2, βE2 and E1 and the macrolide antibiotics (3), and the pesticides methiocarb and neonicotinoids (5)

For groundwater, the quality standards are 100 ng/L for a single pesticide and 500 ng/L for the sum of all individual pesticides detected and quantified in the monitoring procedure, including their relevant metabolites, degradation and reaction products (Directive 2006/118/EC).

Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy, amending and subsequently repealing Council directives 82/176/EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC and amending Directive 2000/60/EC [Official Journal L 348 of 24.12.2008]. Amended by Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013.

Commission implementing Decision (EU) 2015/495 of 20 March 2015 establishing a watch list of substances for Union-wide monitoring in the field of water policy pursuant to Directive 2008/105/EC of the European Parliament and of the Council.

Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration. Amended by Commission Directive 2014/80/EU of 20 June 2014.

5. Human and safety risks

Direct and indirect human impacts should be distinguished when the human impact and safety indicators are assessed (Fig. 5).

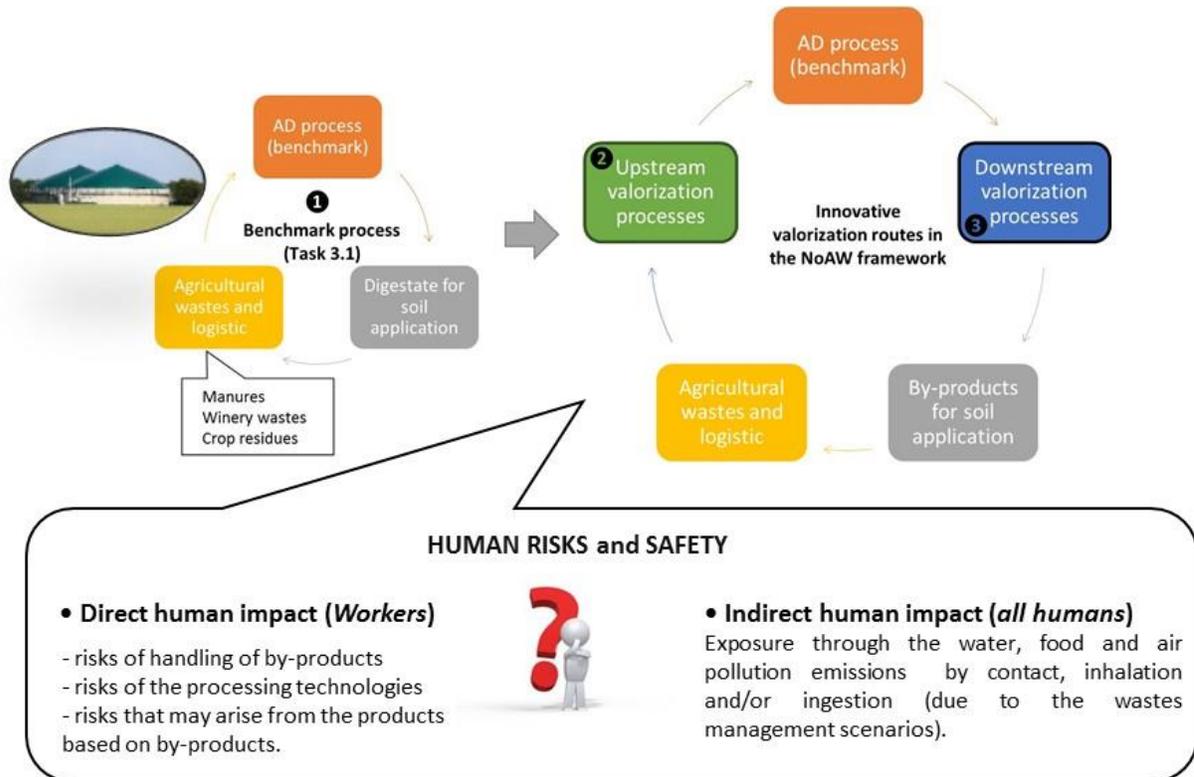


Fig. 5. Direct and Indirect Human Impact assessment of the wastes management processes developed on the NoAW framework.

Direct impacts concern workers, i.e. people directly working with the agricultural wastes considered in the project. Direct impacts can be classified according to the way of exposure along the “agricultural waste value chain”, i.e. through feedstock logistic (including physical risk such as dust explosion or chemical risk such as solvents), the waste conversion process (such as noise and vibrations) or directly by air. Indirect impacts concern all humans. They also can be classified according to the way of exposure, either through air, water and food (such as pesticides), or only through air (such as chemicals, biological, dusts, etc.).

For each human indicator, the impact on human health, the threshold levels as well as the control measures will be described.

5.1. Direct Impacts

5.1.1 Direct impact through feedstock logistic

➤ Dust explosion

Pre-treatment of solid wastes, such as milling, can produce dusts that can explode if mixed with air in a cloud formation and with the presence of an ignition source. Because it can cause serious injuries, the presence of dusts should be one of the indicators for human safety.

Threshold levels

Health and Executive Committee (GB) (last accessed in February, 2017) provides guidelines for the prevention of dust explosions in the food industry. This guideline gives the concentration ranges that can cause explosion and precautions for prevention that can be applied for managing and manipulating dry milled agro-waste. The typical concentration ranges for fine powders that can give rise to an explosion are low from 75 to 1000 g.m⁻³ of air. As a guide, it explains that at these low concentrations it is difficult for an observer to distinguish solid shapes at distances of 60 cm or less.

According to the WHO study (1999), high risk of explosion exists where concentrations of combustible dust exceed 10 g.m⁻³.

Control measures

Workplace directive 99/92/E contains the minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres. It describes the obligation of the employers, which includes risk assessment and classification of areas into zones where hazardous explosive atmospheres may occur and drawing up and keeping up-to date the explosion protection document.

CFPA Guidelines No 31:2013 provides guidelines and measures for protection against self-ignition and explosions in handling and storage silage and highlights that that in normal farming activity the risk of dust explosion is very low and can be controlled by good housekeeping.

Typical examples of preventive measures are the followings: adequate storage and handling, selection and use of vacuum cleaners, pneumatic conveying systems, chokes, sizing of explosion relief vents, ducting explosion relief vents to open air.

• Chemicals

➤ Solvents

Solvents can be used for extraction steps in the valorisation processes of agro-wastes. Most solvents have Occupational Exposure Limits. These limits apply to workers directly involved with tasks using solvents and also to other workers in the workplace who may be exposed to solvents indirectly from these operations. Depending on the type and the concentration of the solvent, they can cause irritation, dizziness, headache, vomiting, kidney problems, or may even be carcinogen. Solvents can produce toxic gases and vapours when they burn or chemically react with other substances. Therefore the presence of solvents can be one of the indicators for human safety (Government of Alberta, 2009).

Threshold levels

Directive 2000/39/EC establishing a first list of indicative occupational exposure limit value for chemical agents. The limit values are given for a reference period of eight-hours time-weighted average (TWA) and short-term exposure (STEL) related to a 15-minute period. DIRECTIVE 2006/15/EC contains additional occupational exposure limit values for further chemicals.

The limits values for some frequently used solvents:

- Diethylether : 8h TWA 308 mg.m⁻³ (100 ppm), STEL 616 mg.m⁻³ (200ppm)
- Acetone : 8h TWA 1 210 mg.m⁻³, (500 ppm), no indicative value for STEL
- (2-Methoxymethylethoxy)-propanol: 308 mg.m⁻³ (50 ppm) no indicative value for STEL
- n-Heptane: 2 085 mg.m⁻³ (500 ppm)
- n-Hexane : 72 mg.m⁻³ (20ppm)
- Methanol : 260 mg.m⁻³ (200 ppm)

Control measures

Control measures for solvents can be the following: use of personal protective equipment, substitution with a less hazardous material, using of engineering controls (e.g. proper ventilation, enclosure around process) and changes in work practices to reduce exposure (Government of Alberta, 2009).

➤ Enzymes

Enzymes can be used for the pre-treatment of different agro-wastes. Enzymes act as catalysts to speed up the chemical reactions in different processes. Skin contact with proteolytic enzymes can cause skin irritation; in this case irritation is caused by properties of the proteases and is not an allergic response. Inhaling high levels of enzyme-containing aerosols may result in coughing and/or congestion due to irritation of the mucous membranes of the respiratory tract. Repeated inhalation of enzyme contained in aerosols can cause an allergic response for the susceptible individuals (simple medical tests are available) but it is not possible to predict who will develop an allergic response.

Enzyme preparations have been used in the manufacture of foods and in industrial processes for many years. Commercial enzymes can be used safely without any adverse health effects through the use of good work practices, so there is no need to include them as specific indicator of human safety.

Threshold levels

American Conference of Governmental Industrial Hygienists (ACGIH) has established a threshold limit value (TLV) for only one class of enzymes, subtilisins, of 60 ng.m⁻³ as a ceiling limit.

Control measures:

There are air-monitoring techniques available to measure the level of enzyme dust or mist in the air. Both low-flow and high-flow air sampling methods are available for some enzymes. For protecting the health of the workers emphasis must be put on safe handling practices, use of personal protective equipment, respiratory protection, protective clothing and gloves.

➤ **Biologicals such as endotoxins**

Different studies showed that in biogas plants - similarly to agricultural activities - during the different operations (biomass storage, loading and unloading) workers could be exposed to bacterial endotoxins. The source of endotoxins is the lipopolysaccharides (LPS) in the cell walls of Gram-negative bacteria derived from decaying wastes. Even low concentrations (200 EU.m^{-3}) can cause the stimulation of the mucous membrane, respiratory diseases up to chronic inflammations of the respiratory system. In biogas plants increased endotoxin concentrations ($> 50 \text{ EU.m}^{-3}$) could be related to operations with aerosol formation (e.g. cleaning activities). In addition, large amounts of agricultural feedstock are often handled in biogas plants and there is a high exposure to inhalable fungal spores and bacteria including actinomycetes in the air at working areas. Both epidemiological and experimental studies confirm that these exposures are associated with development of hypersensitivity pneumonitis, organic dust toxic syndrome, decline in lung function, severity of asthma, respiratory symptoms and airway inflammation (Pietrangeli et al., 2013).

Threshold levels

The threshold levels often expressed in endotoxin units (EU), where one EU equals approximately 0.1 to $0.2 \text{ ng endotoxin.mL}^{-1}$. An exposure limit of 50 EU.m^{-3} has been recommended by ICOH Committee on Organic Dust in 1997 (Pietrangeli et al., 2013). The Dutch Expert Committee on Occupational Standards of the National Health Council has proposed a health-based recommended limit value of 4.5 ng / m^3 (0.45 EU.m^{-3}) over an eight-hour exposure period. (BARTH et al, 2009). The Norwegian 8-h time weighted average (TWA) organic dust occupational exposure limit (OEL) of 5 mg.m^{-3} (Halstensen et al, 2007).

Control measures

Personal protective equipment are the first line of defence in order to prevent the intake via the respiratory tract.

➤ **Microorganisms**

Several pathogens are present in agricultural waste. Getting into contact with a pathogenic organism does not necessary mean that an individual will become ill as it is influenced by several factors such as virulence of the microorganism, susceptibility of the people. Epstein (2008) review that levels of relative hazards of different feedstocks for composting facilities: and summarized that medium to high levels of pathogens can be found in biosolids such as manure. Medium levels of pathogens were found in yard trimmings, which suggest that the NoAW project need to consider this risk for straw and winery waste.

Pathogens can get into the people by different routes. In work environment – like farms, composting facilities, biogas plants - they can cause infection by passing into the people through mouth by the results of unclean hand but such way is rather atypical for occupational infections. Pathogens may also cause infection by inhalation of bioaerosols.

Microbiological risks in manure

Many potential pathogens for livestock as well as humans can be found in manure of both livestock and poultry. These pathogens include bacteria, protozoan and viruses.

The most frequent pathogens in livestock manure include bacteria such as Shiga-toxin producing *Escherichia coli* (*E. coli*), *Salmonella*, *Campylobacter* and *Yersinia*. These bacteria can cause fever, diarrhea, vomiting, nausea, and abdominal pain in humans. Protozoa such as *Giardia* and *Cryptosporidia* can be found in manure and cause illness. Other important aspect, that these protozoa cannot be not easily destroyed from waters except by filtration. Viruses are less frequent but can be present in manure. The most commonly recognized is the rotavirus and these can survive for long periods of time in the environment depending on conditions (Spiehs and Goyal 2007).

Microbiological risks in straw

Most of the workers have some reaction to dusty conditions during harvest, which is made up of both organic and inorganic particles (mould and mould spores, insect parts and excreta, bacteria, endotoxins), which can be inhaled easily. These particles get into the respiratory system causing a range of adverse health effects. The exposure can cause different conditions with very similar symptoms like “Farmer’s Lung” or Hypersensitivity Pneumonitis, which is an allergic reactions or “Organic Dust Toxic Syndrome” which is a toxic reaction.

Microbiological risks in winery waste

Pathogens may be presented in winery waste. Bustamante et al., (2007) monitored some microbial indicators and pathogen content (sulphite reducing clostridia, total enterobacteriaceae, total coliforms, *Escherichia coli*, enterococci, *Staphylococcus aureus* and *Salmonella* spp.) in winery waste to evaluate the effectiveness of the composting process in reducing the pathogen content.

Threshold levels

DIRECTIVE 2000/54/EC provide a list of agents, which are known to infect humans and classify them based on the effect on healthy worker but in these document qualitative only aspects can be found.

There are no existing guidelines for community levels, but a number of countries published occupational limit values. The following levels are acceptable but these are guidelines and not based upon dose-response relationships or health measures. Pearson et al. (2015)

- 1000 cfu.m⁻³ for total bacteria.
- 300 cfu.m⁻³ for gram-negative bacteria
- 500 cfu.m⁻³ for *Aspergillus fumigatus*

Control measures

DIRECTIVE 2000/54/EC lays down the minimum requirements of protecting workers against risks to their health and safety, including risk assessment, the prevention of such risks, arising or likely to arise from exposure to biological agents at work.

It highlights the importance of replacement harmful biological agent if feasible, reduction of risks, applying following the good hygiene practices, providing individual protection and keeping workers informed and trained.

5.1.2 Direct impacts through waste conversion processes

➤ Noise

Noise related hearing loss were identified as major issues for the operators in AD plants. The main source of high noise levels is the engine generator set. Decibel (dB) levels produced at an AD facility will differ due to varying acoustical settings, but a general set can produce between 100 – 140 dB. (Agstar, 2011).

Exposure to high levels of noise can result in discomfort or short-term hearing loss. In extreme cases, or if the noise exposure occurs over a long period of time, permanent hearing loss can occur (Directive 2003/10/EC).

Threshold levels

Noise exposure limits values are defined in Directive 2003/10/EC. Besides the exposure limit values it defines the action values, which are once exceeded, the employer must implement an action plan to prevent exposure from exceeding the exposure limit values.

The daily noise exposure limit value is 87 dB for a nominal eight-hour working day. The peak sound pressure (maximum value of the "C"-frequency weighted instantaneous noise pressure) is 200 Pa. The upper exposure action values are 85 dB (for 8 hours) and 140 Pa peak sound pressure respectively.

In Agstar Guideline (2011), which is specific for anaerobic digestions, shows the safe allowable decibel levels are indicated for noise. These were established by OSHA and measured with a sound level meter set on slow response. The safe maximum allowable decibel level is defined as 90 dB for 8 h but if the noise level increases the safe maximum allowable level decreases e.g. 90 dB for 8h, 95 dB for 4h, 105 dB for 1h.

Control measures

Use of personal protective equipment is advised to reduce exposure to noise.

➤ Vibration

Hand arm vibrations were identified as one of the major issues for the operators in AD plants. Using vibrating tools, handling vibrating machine controls, or sitting on vibrating equipment can cause exposure. (e.g. grinding, employing engines, abrasive actions, etc.). Vibration is the oscillation of a body about a reference point. The number of oscillations per second gives the frequency of vibration (Hz). Vibration can be felt as it is transmitted through solid structures directly to the human body. Prolonged vibration can produce damage to tiny nerves and blood vessels.

Threshold levels

Directive 2002/44/EC describes the minimum health and safety requirements regarding the exposure of workers to the risks arising from physical agents. Besides the exposure limit values it defines the action values, which are once exceeded, the employer must implement an action plan to prevent exposure from exceeding the exposure limit values. Measurement of hand-arm vibration is also described in Directive 2002/44/EC.

For hand-arm vibration the daily exposure limit value standardised to an eight-hour reference period is $5 \text{ m}\cdot\text{s}^{-2}$; while the daily exposure action value standardised to an eight-hour reference period is $2.5 \text{ m}\cdot\text{s}^{-2}$. For whole-body vibration the daily exposure limit value standardised to an eight-hour reference period

is 1,15 m/s², while the daily exposure action value standardised to an eight-hour reference period is 0.5 m.s⁻².

Control measures

Padded or gel-filled gloves for vibrating tools or machine controls should be used. The use good seat cushions and proper seat shape to protect the lower back can reduce the exposure to vibration. Plan must be prepared for breaks and recovery/rest periods.

➤ Cold and heat stresses

Workers in waste management activities are subject to the hazards generally associated with performing physical labour near large equipment or in an outdoor environment including extreme heat and cold fatigue. Searl and Crawford (2012) explained that when an individual's core temperature increases, the blood available has to both transport oxygen and transport heat from the body core. This results in a limitation on the level of oxygen available as temperature regulation appears to have priority over oxygen transport. Heat stress occurs when the body is subjected to temperatures that cause the core temperature to stay above 38°C, over the course of the workday. The heat stress can lead to related disorders such as fainting, prickly heat rash, heat exhaustion and heat stroke. The upper limit for optimal mental performance is 25°C.

The most likely situations where cold stress could happen are where employees are working outside in winter or in wet conditions. In cold working environment workers face the risk of hypothermia, even to the point of frostbite.

Threshold levels

Directive 89/391 describes the minimum safety and health requirements for the workplace. The temperature during working hours must be adequate for human beings, having regard to the working methods being used and the physical demands placed on the workers. Many countries took additional measures to raise the level of implementation and understanding or issued further regulations with higher level of details (EC, 2012).

Some national regulation or recommendations only specify minimum temperature requirements, while others give upper limits for the work temperature. As an example, in Spain it is 27°C for sedentary and 24°C for light work, while in Finland it is 25°C and 23°C accordingly.

Health and Safety Executive (HSE, UK) does not have specific guidance for working in temperatures below 13°C but suggests standards that provide a framework for protection of workers.

- BS 7915:1998, Ergonomics of the thermal environment. Guide to design and evaluation of working practices for cold indoor environments,
- BS EN ISO 15743:2008, Ergonomics of the thermal environment. Cold workplaces. Risk assessment and management,
- BS EN 511:1994, Specification for protective gloves against cold.

As an example, the 4/2002. (II. 8.) SZCSM–EüM Hungarian regulation describes that a workplace is qualified as being « cold » if the temperature does not reaches 4°C for the 50% of the working hours in open air or 10°C for the 50% of the working hours in closed environment.

Control measures

Different practices can help to reduce the effects of the heat stress or assist in acclimation, such as fluid replacement, providing accurate verbal and written instructions and training on heat stress, diet and life-style guidelines that can the risks of heat stroke.

The cold exposure can be decreased by wearing protective equipment such as appropriate clothing, mittens or gloves. Dehydration can occur in a cold environment and may increase the susceptibility of the worker to injury due to a change in blood flow to the extremities. Warm sweet drinks and soups should be consumed to provide caloric intake and fluids. Adequate planning of work (not too much standing or sitting in cold) is essential.

5.1.3 Direct impacts through air

➤ Carbon monoxide (CO)

Breathing CO can cause headache, dizziness, vomiting, and nausea. If CO levels are high enough, it can cause unconsciousness or death. Exposure to moderate and high levels of CO over long periods of time has also been linked with increased risk of heart disease. ([tps://ephtracking.cdc.gov/show-CoRisk](https://ephtracking.cdc.gov/show-CoRisk)).

Threshold levels in air

Directive 2008/50/EC shows the limit for carbon monoxide. It is given as a daily eight hour mean and its maximum is 10 mg.m^{-3} .

Hunter at al. (1999) collected and summarized the occupational exposure limits for chemicals in the European Union. For carbon monoxide, the following values were shown: 23 mg.m^{-3} (20 ppm) for the 8 hour Time Weighted Average exposure limit and 117 mg.m^{-3} (100 ppm) for the Short Term Exposure Limit (STEL-15 mins).

Control measures

Test air regularly in areas where CO may be present, including confined spaces. Install CO monitors with audible alarms. Use a full-facepiece pressure-demand self-contained breathing apparatus. Use respirators with appropriate canisters for short periods under certain circumstances, where CO levels are not exceedingly high. Educate workers about the sources and conditions that may result in CO poisoning as well as the symptoms and control of CO exposure (OSHA, 2002).

On-Site Sampling Techniques/Methods: OSHA recommended method is using electrochemical sensor, which has data logger and sampling information up to 8 hours with detection limit: 4.1 ppm.

5.2. Indirect Impacts through air, water and food

➤ Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs), which are genotoxic and carcinogenic agents, can contaminate foods by different ways. The most frequent ways of contamination are smoking, heating and drying processes that allow the combustion of products. In Regulation (EC) No 1881/2006 it is described that PAHs were considered in 2002 by the Scientific Committee on Food (SCF) as being genotoxic carcinogens. The effects on human health depend on the length and route of exposure. The long-term effect of

PAHs may include decreased immune function, cataracts, kidney and liver damage, breathing problems, asthma-like symptoms, and lung function abnormalities.

According to the SCF, benzo(a)pyrene can be used as a marker for the occurrence and effect of carcinogenic PAH in food, including also benz(a)anthracene, benzo(b)fluoranthene, enzo(j)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene, cyclopenta(c,d)pyrene, dibenz(a,h)anthracene, dibenzo(a,e)pyrene, dibenzo(a,h)pyrene, dibenzo(a,i)pyrene, ibenzo(a,l)pyrene, indeno(1,2,3-cd)pyrene and 5-methylchrysene (No 1881/2006).

Threshold levels in air

PAH generation through agricultural sources can be the result of the burning of organic materials under suboptimum combustion conditions.

Target value for benzo(a)pyrene in ambient air (DIRECTIVE 2004/107/EC) is 1 ng.m^{-3} (for the total fraction in the PM10 fraction averaged over a calendar year).

Threshold levels in water

World Health Organization (2003) summarized the concerns related to PAHs in drinking water. It describes that apart from highly industrially polluted rivers, the concentrations of individual PAHs in surface and coastal waters are generally $\approx 50 \text{ ng.L}^{-1}$. PAH levels in uncontaminated groundwater are usually in the range of $0\text{--}5 \text{ ng.L}^{-1}$. Leaching of PAHs from soils into groundwater is negligible, as the compounds tend to adsorb strongly to the soil organic matter. Elevated concentrations of PAHs (predominantly FA, BbFA, PY, IP, phenanthrene) were observed in rainwater and especially in snow and fog. The typical concentration range for the sum of the selected PAHs in drinking-water is from about 1 ng.L^{-1} to worst cases of $11 \text{ }\mu\text{g.L}^{-1}$. According to the WHO guideline the main source of PAH contamination in drinking-water is usually not the raw water sources but the coating of the drinking-water distribution pipes.

The threshold limits for water intended for human consumption is regulated in Council Directive 98/83/EC. It sets the individual parametric value for benzo(a)pyrene to the $0,010 \text{ }\mu\text{g.L}^{-1}$.

Threshold levels in food

Smoking and heating processes can cause PAH contamination of foods but environmental pollution may cause contamination with PAH, in particular in fish and fishery products.

The EC No 1881/2006 regulation presents the maximum levels of PAHs for different types of products. The limit values are given for benzo(a)pyrene and for the sum of benzo(a)-pyrene, benz(a)anthracene, benzo(b)fluoranthene and chrysene. The permitted maximum levels vary between around $5\text{--}6 \text{ }\mu\text{g.kg}^{-1}$ of benzo(a)-pyrene for smoked fish products and $3\text{--}5 \text{ }\mu\text{g.kg}^{-1}$ of benzo(a)-pyrene for cocoa fibres and cocoa beans derived products (measured in $\mu\text{g.kg}^{-1}$ fat). For specific target groups like infants, babies, medical products has to comply much lower limit values, it is set to maximum $1 \text{ }\mu\text{g.kg}^{-1}$ benzo(a)-pyrene.

Control measures

In developing a food safety management system based on HACCP principles, it is important to identify PAHs as a potential hazard and the risk of their occurrence needs to be controlled. Food business needs to identify any CCPs in their processes, such as combustion products and drying processes, that may be a source of PAH formation. For the general public it is suggested to avoid direct contact of oil seeds or cereals with combustion products during drying processes, to avoid contact of foods with flames when

barbecuing, to use less fat for grilling and cook at lower temperatures for a longer time (Food Safety Authority of Ireland, 2015).

➤ Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) are a group of 209 different congeners, which can be divided into two groups according to their toxicological properties: 12 congener's exhibit toxicological properties similar to dioxins and are therefore often termed dioxin-like PCBs. The other PCBs do not exhibit dioxin-like toxicity but have a different toxicological profile (No 1881/2006).

PCBs persist in the environment the reason for it their unreactiveness and the fact that they are largely resistant to breakdown by acids, bases and heat. It belongs to the group of persistent organic pollutants (POPs). Generally, PCBs are not very soluble in water, but readily soluble in fats this is the reason why PCBs can build up in animal fat and along the food chain. (Green Facts, last accessed in March, 2017). The critical endpoints for risk assessment of PCBs are identified as cancer, immunotoxic, neurotoxic, hepatotoxic, and toxic to reproduction and behavioural effects.

Threshold levels in air

Few studies have been conducted to measure ambient air levels of PCBs, but concentrations appear to differ markedly between locations such as type of areas or place of measurement. The lowest levels, from 0.002 ng.m^{-3} , are found in non-industrialized and non-contaminated areas, while industrialized zones may have higher levels such as 3.3 ng.m^{-3} (for example in the Ruhr area in Germany). Nearby industrial plants the levels can reach 45 and $650 \text{ } \mu\text{g.m}^{-3}$ (WHO, 2000).

Threshold levels in water

The threshold limits for water intended for human consumption is regulated in Council Directive 98/83/EC but it does not contains specific parametric value for PCBs (just for other chlorinated compounds).

Industrial discharges are prohibited under the Clean Water Act Effluent Guidelines (EPA, U.S.). The PCB spills or accidental releases into the environment of 1 pound or more are needed to be reported to EPA. EPA's goal for drinking water's maximum contaminant level is zero, and the enforceable MCL (maximum contaminant level) for PCBs in public water systems is 0.0005ppm.

Threshold levels in food

For the general public the food is the main source of exposure to PCBs. Exposure occurs primarily by ingesting high-fat foods—such as dairy products, eggs, and animal fats—and some fish and wildlife. Levels reported in drinking-water are typically between 0.1 and 0.5 ng.L^{-1} (WHO, 2000).

The Food and Agriculture Organization (FAO) and the World Health Organization (WHO) allow a daily PCB intake of $6 \text{ } \mu\text{g.kg}^{-1}$ per day (ATSDR, last accessed in March 2017).

The specific limit values for different product types can be found in EC No 1881/2006 regulation. There are differences in threshold limits by product type, terrestrial animals vs. fishery products, target groups (e.g. foods for infants and young children).

Control measures

In order to reduce the contamination of food, the following control measures need to be considered: developing Good Agricultural Practice, Good Animal Feeding Practice and Good Manufacturing Practice. Some examples: do not use contaminated soil / areas for production of feed crops, sewage sludge used in agriculture should be monitored for fulfilling the the threshold levels, animal derived feed should be monitored for dioxins, control critical feed manufacturing processes (e.g., drying , heating) (FAO, 2008).

➤ Veterinary medicines

The pathways that are in the focus of NoAW project is the excretion of substances in urine and feces of livestock animals, and the wash-off of topical treatments from livestock animals. Drug residues may cause adverse effects in humans. The potential adverse reactions, effects on human intestinal flora and allergic reactions are most likely following oral exposure (Baynes et al. 2015). Other studies also confirmed the link between antibacterial use in agriculture and antibacterial-resistant infections, and there is evidence that antibacterial resistance from agriculture can be transferred to humans (Boxall, Kolpin, Halling – Sørensen 2003). Beyene (2016) highlighted that drug low-level contamination generally may not generate a violation problem on public health. However, extensive use of drugs may increase the risk of an adverse effect of residues on the customer including the occurrence of antibiotic resistance and hypersensitivity reaction.

Threshold levels in air

Less important route for emission of veterinary medicines is through air although some studies investigated the potential of the contamination by bioaerosols and dust (Boxall, Kolpin, Halling – Sørensen, 2003).

Threshold levels in water

WHO (2012) evaluated the presence of pharmaceuticals in drinking water. The summarized studies have shown that concentrations of pharmaceuticals:

- in surface water and groundwater sources impacted by wastewater discharges are typically less than $0.1 \mu\text{g}\cdot\text{L}^{-1}$ (or $100 \text{ ng}\cdot\text{L}^{-1}$)
- concentrations in treated drinking-water are usually well below $0.05 \mu\text{g}/\text{l}$ (or $50 \text{ ng}/\text{l}$).

There are few comprehensive, systematic studies on the occurrence of pharmaceuticals in drinking-water and limited data is available assess the potential risk for human health.

Threshold levels in food

Veterinary drugs, the maximum residues limits (MRLs) are derived by JECFA (Joint FAO/WHO Expert Committee on Food Additives) from controlled residue depletion studies.

The current practice for veterinary drug residues is to use a set “food basket” (consisting of 300 g muscle, 100 g liver, 50 g kidney, 50 g fat, 1500 g milk, 100 g eggs and 20 g honey) to derive an estimate of potential dietary exposure; at an international level, this estimate cannot be refined, although at a national level, further refinement may be possible. (FAO, UN, WHO, 2009)

EU regulation No 37/2010 contains information on maximum residue limits of pharmacologically active substances and their classification regarding in foodstuffs of animal origin.

Control measures

Pharmaceuticals in drinking water are not unusual organic chemicals, and treatment removal rates depend on the physical and chemical properties. They describe that conventional treatment processes with chlorination (free chlorine) can remove about 50% of these compounds. Advanced water treatment processes are more effective can remove more than 99% of large pharmaceutical molecules. These treatments can include the following technologies: ozonation, advanced oxidation, activated carbon and membranes (e.g. reverse osmosis, nanofiltration) (WHO, 2012).

Preventive measures can reduce the contamination of environment. Some examples to promote proper disposal of medicines and reduce the impact of pharmaceuticals: policies promoting or regulations governing disposal practices at concentrated point sources (e.g. health-care and veterinary facilities), take-back programmes, guidance and enhanced consumer education (WHO 2011).

➤ Pesticides

Pesticides are widely used in agricultural production to prevent or control pests, diseases, weeds, and other plant pathogens in an effort to reduce or eliminate yield losses and maintain high product quality. Due to their high biological activity, and, in some cases, long persistence in the environment, pesticides may cause harmful effects to human health and to the environment (Damalas- Eleftherohorinos, 2011).

Non-occupational exposure originating from pesticide residues in food, air and drinking water generally involves low doses and is chronic (or semi-chronic). However, clear links between individual pesticides and individual health effects can only be shown in animal studies, but the doses used in these studies are far higher than the enforced legally pesticide limits (Damalas - Koutroubas, 2016).

Threshold levels in air

Pesticides can get into the air with fumigants (gasses), dusts or when liquid pesticides are applied as a very fine mist. Drift likely to occur on windy days and when temperatures are very high. Pesticides in the air can rise to very high altitudes and move for long distances attached to particles. There are no threshold levels in the regulation for ambient air (DIRECTIVE 2004/107/EC and DIRECTIVE 2008/50/EC).

Threshold levels in water

Pesticides can get into water via drift during pesticide spraying, by runoff from treated area, leaching through the soil. In some cases pesticides can be applied directly onto water surface e.g. for control of mosquitoes. Water contamination depends mainly on nature of pesticides (water solubility, hydrophobicity), soil properties, weather conditions, landscape and also on the distance from an application site to a water source. Rapid transport to groundwater may be caused by heavy rainfall shortly after application of the pesticide to wet soils.

The threshold limits for water intended for human consumption is regulated in Council Directive 98/83/EC. It sets the individual parametric value for pesticides $0.10 \mu\text{g.L}^{-1}$, for total pesticide content $0.50 \mu\text{g.L}^{-1}$.

Threshold levels in food

The European Commission fixes Maximum Residue Levels (MRLs) for all food and animal feed. The MRLs for all crops and all pesticides can be found in the MRL database on the Commission website (EU Pesticide database).

The MRLs for those pesticides which were reported as most frequently detected in table and wine grapes are the followings for wine grapes: dithiocarbamates 5 mg.kg⁻¹, ethephon 1 mg.kg⁻¹, fenhexamid 15 mg/kg, boscalid 5 mg/kg, dimethomorph (sum of isomers) 3 mg.kg⁻¹.

The MRLs for those pesticides which were reported as most frequently detected for wheat are the followings : Chloromequat 2 mg.kg⁻¹, Chlorpyrifos-methyl (F) 3 mg kg⁻¹, Glyphosate 10 mg.kg⁻¹, Pirimiphos-methyl (F) 5(ft) mg.kg⁻¹, Tebuconazole (R) 0,3 mg/kg, Deltamethrin (cis-deltamethrin) (F) 2mg.kg⁻¹, Mepiquat (sum of mepiquat and its salts, expressed as mepiquat chloride) 3 mg.kg⁻¹.

Control measures

Good Agricultural Practice can reduce exposure to pesticides. If the main aspects are kept, the contamination of the environment / potentially harmful residues on the crop can be prevented. It is essential to use permitted pesticide products, and only on crops specified and for weeds or pests indicated on the label. Application rates and recommendation for usage must be kept and the equipment need to checked / calibrated regularly in order to deliver the correct rate. Pesticides must be applied under the right environmental conditions to reduce the possibility of spray drift, run-off or leaching that may contaminate other crops. Appropriate clean instructions are needed for equipment to prevent carry over and contamination. The pre-harvest interval and the pre-grazing interval requirements must be followed.

Farmers and farm workers face greater risk of exposure to pesticides than typical non-agricultural workers, comprising a major group of workers that are consistently exposed to pesticides. The exposure of workers increases in the case of not paying attention to the instructions on how to use the pesticides and particularly when they ignore basic safety guidelines on the use of personal protective equipment and fundamental sanitation practices such as washing hands after pesticide handling or before eating. Training on good practice is essential.

➤ Heavy metals

Heavy metals can be potentially toxic chemical elements that are present in the environment, soil and in food products. The most frequent ways of human exposure is by ingestion (drinking or eating) or inhalation (breathing). The toxicity of these elements depends on several factors such as dose, route of exposure, and chemical species, on human dependent factors like age, gender, genetics, and nutritional status of exposed individuals (Tchounwou et al, 2014). Arsenic, cadmium, chromium, lead and mercury have the greatest potential to cause risk for human because of their high degree of toxicity and extensive use. These elements are carcinogen and cause serve damage in human organs (lung, kidneys, lungs, nerve system) even in low exposure levels. High levels can cause irritating stomach, vomiting breathing problems (e.g.: cadmium, chromium VI compounds, mercury vapour) or immediate death because of serve damage of brain or other organs (e.g. arsenic, lead, methyl -mercury). Plants and animals can accumulate heavy metals from the environment. Humans are more likely to be exposed to heavy metals by the soil itself that sticks to the plant and hard to remove. Fish, especially bottom eater species can accumulate higher amounts from water they live in and also from the sediment (Martin and Griswold, 2009).

Threshold levels in air

Exposure to heavy metals can happen through inhalation. Different studied showed the heavy metals concentration such as arsenic can vary by location: the exposure in remote locations 1 to 3 ng/m³, while in cities 20 to 100 ng.m⁻³ in cities. Individuals can be exposed to heavy metals such as cadmium or lead via inhalation of smoke, cigarette, dust particles and aerosols. (Tchounwou et al, 2014):

The heavy metal threshold limits for air can be found in DIRECTIVE 2004/107/EC and DIRECTIVE 2008/50/EC. The target values for the total content in the PM10 fraction averaged over a calendar year are 6 ng.m⁻³ Arsenic, 5 ng.m⁻³ Cadmium, 20 ng.m⁻³ Nickel.

Threshold levels in water

Water contains less than 10 µg.L⁻¹ arsenic although higher levels can occur near natural mineral deposits. The typical concentration of chromium in sea water 5 to 800 µg.L⁻¹, and 26 µg.L⁻¹ to 5.2 mg.L⁻¹ in rivers and lakes. Cadmium, lead and mercury exposure can happen by consumption of contaminated water (Tchounwou et al, 2014).

The threshold limits for water intended for human consumption is regulated in Council Directive 98/83/EC. It sets the following limits for the above mentioned heavy metals: 10 µg/l Arsenic, 5,0 µg/l Cadmium, 50 µg.L⁻¹ Chromium, 10 µg.L⁻¹ Lead, 1.0 µg.L⁻¹ Mercury.

The limit value for lead is 0.5 µg.m⁻³ (averaging period is a calendar year).

Threshold levels in food

Exposure to heavy metals can happen through inhalation. Different studies showed the heavy metals concentration such as arsenic can vary by location: the exposure in remote locations 1 to 3 ng/m³, while in cities 20 to 100 ng.m⁻³ in cities. Individuals can be exposed to heavy metals such as cadmium or lead via inhalation of smoke, cigarette, dust particles and aerosols (Tchounwou et al, 2014).

Arsenic ranges in foods from 20 to 140 ng.kg⁻¹. The typical concentration of chromium for fresh food is <10 to 1 300 µg.kg⁻¹. Mercury, cadmium also can accumulate in seafood and fishes (Tchounwou et al, 2014).

The EC No 1881/2006 regulation contains the complete list for different foods. For this summary we focused on the products that can be relevant for the NoAW project (animal, wheat / grain and grape based products – where available). Threshold for lead may vary between 0.02 and 0.5 mg.kg⁻¹ wet weight depending on type of the food. This threshold for cadmium can range from 0.05 to 0.2 mg.kg⁻¹ wet weight, for mercury from 0.1 to 1 mg.kg⁻¹ wet weight, for arsenic from 0.25 to 0.3 mg.kg⁻¹ wet weight. For specific limit values, to check the detailed list of EC No 1881/2006.

Control measures

FSAI (2009) describes the importance of use of control measures.

Companies should identify critical control points (CCPs) in their processes such as lead in the water supply.

The identification of appropriate CCPs along their process chain will enable them to develop and apply proper HACCP systems, which will ensure that there are no unforeseen sources of metal contamination in the food.

➤ Ammonia

At room temperature the ammonia is colourless, pungent and flammable gas. Ammonia is a severe irritant for eye, skin, respiratory track, chronic exposure induce irritation, coughing, and difficult breath. 30 - 40 ppm cause irritation of mucous membranes, respiratory tract and eyes, more than 300 ppm constitute immediate danger towards life and health (NOISH/ National Institute for Occupational Safety and Health). 1000 ppm can cause difficulty in breathing and unconsciousness. Danger of fire is in the range 15 % - 30 %.

Threshold levels in air

DIRECTIVE 2008/50/EC which regulates ambient air quality does not contain threshold limits for ammonia.

2000/39/EC establishing the indicative occupational exposure limit values for the protection of the health and safety of workers from the risks related to chemical agents. For ammonia the 8 hours exposure limit values is 14 mg.m^{-3} (20 ppm), while the short term exposure is limited to 36 mg/m^3 (50 ppm).

Control measures

The following solutions, action can reduce the risk related to ammonia: process enclosure, local exhaust ventilation, general dilution ventilation and personal protective equipment. Airborne ammonia can be determined by monitoring sulphuric acid impregnated carbon bead tubes (USA department of Health and Human services, 1992).

As a minimum it is recommended protective gloves, splash-proof goggles, hearing protection, and steel toe shoes for employees associated with the digester system. For visitors to the facility, safety glasses and hearing protection should be available and worn while on site. In case of ammonia, leak persons not wearing protective equipment should be restricted from the area.

➤ Nitrogen oxides

Nitrogen oxides are produced during combustion, especially at high temperature. In addition to acting as a main precursor for tropospheric ozone, which is toxic in high concentration, NO_x are also harmful to human health in its own right.

Once in the bloodstream, NO binds to haemoglobin, which is probably responsible for the absence of systemic effects of inhaled NO. After combining with a specific receptor, it relaxes smooth muscle in blood vessel walls, leading to vasodilation (SCOEL, January 2003).

Effect of NO₂ is irritation of the deep compartment of the respiratory tract in both animals and man. NO₂ is well absorbed via the lungs. It is then likely to be incorporated into intermediary metabolism pathways and does not result in systemic effects (SCOEL, 2014). This substance has an irritating odour; its odour threshold ranges between 0.2 and 0.8 mg.m^{-3} (0.10-0.41 ppm).

Nitrogen oxides in contact with water result in the production of acids (like nitric acids). It can cause problems both in industry and agricultural areas. These are irritants that cause burning feeling on skin, respiratory system and cause dizziness and headache.

Thresholds in air

Directive 2008/50/EC shows the limit for NO₂. It is given as a daily 8-hour mean and its maximum is set at 10 mg.m^{-3} . SCOEL (2014) recommendation is lower, with the 8-hour exposure limit set at 0.5 ppm. For one hour of exposure, its maximum limit value is $200 \text{ }\mu\text{g.m}^{-3}$, and this cannot be exceeded more than 18 times per calendar year. For a calendar year, its maximum limit value is $40 \text{ }\mu\text{g.m}^{-3}$.

Suggested limits for general population based on WHO (Dutch Expert Committee on Occupational Standards, 2004) are the same as in the Directive 2008/50/EC.

In terms of NO_x, Directive 2008/50/EC gives limits only for the protection of vegetation, which is $30 \text{ }\mu\text{g.m}^{-3}$ for a calendar year.

Control measures

The installation of special oxidizers that treat the unburned fumes that are rich in CO and NO_x are currently required. Multi-gas detectors can be used for the determination of NO_x contents.

➤ Hydrogen sulphide

Hydrogen sulphide is an asphyxiant chemical, which means that it prevents the uptake of oxygen into human cells. Hydrogen sulphide is dangerous because it reduces the body's ability to absorb, transport, or utilize inhaled oxygen. Asphyxiant gases are present wherever there is storage of an organic material; therefore, manure pits or any other areas for organic material storage become potentially dangerous (AgSTAR, 2011). Hydrogen sulphide is a colourless gas with a strong odour of "rotten eggs". The substance is flammable and explosive in air and may even be ignited by static discharge (SCOEL, 2007). The odour threshold of hydrogen sulphide (H₂S) is 0.18 mg.m⁻³ (0.13 ppm). We are faced to an immediate danger if hydrogen sulphide content is above 100 ppm. It is worth noting that at concentrations higher than 100 ppm (140 mg.m⁻³), humans are not able to smell H₂S, probably due to olfactory fatigue (SCOEL, 2007).

Threshold levels in air

The WHO air quality guideline suggests for hydrogen sulphide is 150 µg.m⁻³ for an average concentration over 24 hours. To avoid odour annoyance, a 30-min average ambient air concentration not exceeding 7 µg.m⁻³ is recommended (WHO, 2003).

The recommendation of the Scientific Committee on occupational exposure limits is 14 mg.m⁻³ (10 ppm) for short term (STEL) and 7 mg.m⁻³ (5 ppm) for 8 hours (total weighted average).

SCOEL documents describe that in industrial environments where humans are exposed to short-term durations, a STEL of 10 ppm is recommended. They also mention that it is strongly advised to avoid exposure to rapid rising high peaks.

Threshold levels in water

It is unlikely that anyone could consume a harmful dose of hydrogen sulphide in drinking-water and for this reason no health-based guideline was proposed (WHO, 2003).

Control measures

The level of H₂S can be measured with handheld or wall mounted multi-gas detectors. In the event that a hazardous gas sensor is triggered, the emergency action plan should be implemented. As a minimum it recommends protective gloves, splash-proof goggles, hearing protection, and steel toe shoes for employees associated with the digester system. For visitors to the facility, safety glasses and hearing protection should be available and worn while on site.

➤ Biologicals such as bioaerosols

Although bioaerosols are present everywhere, in the waste management operation the level of the bioaerosols are higher due to specific feature of the process, which requires micro-organisms to support the and contains specific activities such as shredding, turning, which release the micro-organisms into the air. The can be an important indicator as aerodynamic properties allow them to be released at high numbers on site, but also potentially travel away from site, downwind. (Drew et al., 2009) Biological

agents that are transmitted as bioaerosols are of the greatest epidemiological importance. As Gróny (last accessed 2017) explains the type of interactions between the bioaerosol particles and human cells depends on the place of their deposition and is conditioned by their retention time in the respiratory tract. The health effects include but are not limited to inflammatory and allergic respiratory diseases, eye and skin irritations but it can cause infectious aspergillosis, zygomycosis. Besides, it has to be emphasized those special groups e.g.: immunocompromised individuals are more susceptible at lower concentrations of the relevant pathogens in bioaerosols.

Threshold levels in air

According to Pearson et al. (2015) there are no apparent existing guidelines for community levels in other countries, but a number of countries published occupational limit values. The following levels are acceptable but these are guidelines and not based upon dose-response relationships or health measures.

- 1000 cfu.m⁻³ for total bacteria.
- 300 cfu.m⁻³ for gram-negative bacteria
- 500 cfu.m⁻³ for *Aspergillus fumigatus*.

The bioaerosols vary greatly depending on season, time of day, geographic location, and local weather conditions (particularly humidity and solar radiation). In the literature very different values can be found concerning the distance to which waste management (e.g: composting) bioaerosols can be detected: it ranges from 150 m to 1400 m. The UK Environmental Agency considers that concentrations can return to those of the background noise as near as 250m from the source emission but Wéry (2014) suggests extending this range to 500 m.

Control measures

For the general public if the facility is more than 500 m from the living environment, the bioaerosol exposure can be negligible. In working environment the recommended measures include the use of:

- Vehicles with sealed cabs with air filtration and doors and windows which must be closed during operations with compost or appropriate respiratory protective equipment employed.
- Elevators, conveyors and screens should be enclosed or fitted with extraction.
- Respiratory protective equipment should be used where exposure to airborne dust is unavoidable.

➤ Dust

Employees and local residents can be exposed to dust generated in the whole value chain (e.g. handling & transporting feedstock, carrying out different process steps such as moulding, etc.). The particle matter (PM) can be a good indicator for benchmarking of different agricultural waste management strategies. The inhalable particles can be divided into two main groups:

- coarse particles with a diameter between 2.5 and 10 µm (PM10)
- fine particles with a diameter of 2.5 µm or less (PM2.5)

The dust exposure can cause respiratory and lung diseases. The particles are deposited, either in the head or in the lung; they have the potential to cause harm either locally or subsequently elsewhere in the body. The deposition of particulates in different parts of the human respiratory system depends on particle size, shape, density, and individual breathing patterns. All particles smaller than 10 microns in

diameter can reach the human lungs, the retention rate is largest for the finer particle (Airborne Particulate Matter, World Bank Group 1998).

Exposure to fine particles (PM_{2.5}) can have short- or long-term effect. Even the short-term exposure can have health effects like eye, nose, throat and lung irritation, coughing, sneezing, runny nose and shortness of breath. Long-term exposure to fine particulate matter can be linked to increased rates of chronic bronchitis, reduced lung function and increased mortality from lung cancer and heart disease.

Threshold levels in air

Pollution by small particulates has an impact on health even at very low concentrations – indeed no threshold has been identified below which no damage to health is observed (WHO, 2016).

The 2005 "WHO Air quality guidelines" offer global guidance on thresholds and limits for key air pollutants that pose health risks. In case of PM₁₀ the annual mean is 20 µg.m⁻³, and the 24-hour mean is 50 µg.m⁻³. The annual mean limit for PM_{2.5} is 10 µg.m⁻³, while the 24-hour mean is 25µg.m⁻³.

Directive 2008/50/EC limits PM₁₀ to 50 µg.m⁻³ for yearly average and 50 µg.m⁻³ for one day (not to be exceeded more than 35 times for a calendar year, limit value entered into force in 2005).

The limit for PM_{2.5} entered into force in 2015. It specifies the limit value for only for yearly average, which is 25 µg.m⁻³. No one-day limit value is available.

Control measures

Changing processes and activities can help to reduce dust at source, for example enclosure of the process, good general ventilation, proper handling of materials; good maintenance of plant and equipment, and good housekeeping.

Control measures for occupational dust exposures: risk assessment should be carried out and protective equipment, specific design such as the use of screeners, dust suppression equipment, front-end loaders needs to be taken into consideration. Exposition should be checked regularly.

6. Conclusions and perspectives

In the **task 1.5**, the various partners have worked on the identification of key indicators for assessing the impact of the waste management routes developed within the NoAW framework on the environment and human safety. This work in the first assessment of the sustainability of the processes developed under the NoAW framework and will be completed in other tasks by economic and social indicators, which represent with environmental indicators the three items of the sustainability.

In parallel, the methodologies that will be used for assessing these indicators have also been explained. The main results and methodologies have been presented in the deliverable 1.5. The main conclusions are the following ones:

- Several sustainability indicators have been developed to assess the impact on environment on the various items: soil; air, water and human risks and safety as shown in **Fig.6**.
- Human safety and risk indicators have also been assessed and threshold limits in air, water and food items have been provided according the indicators (**Fig.6**). Such indicators will be incremented with other social indicators that will be developed during the project.

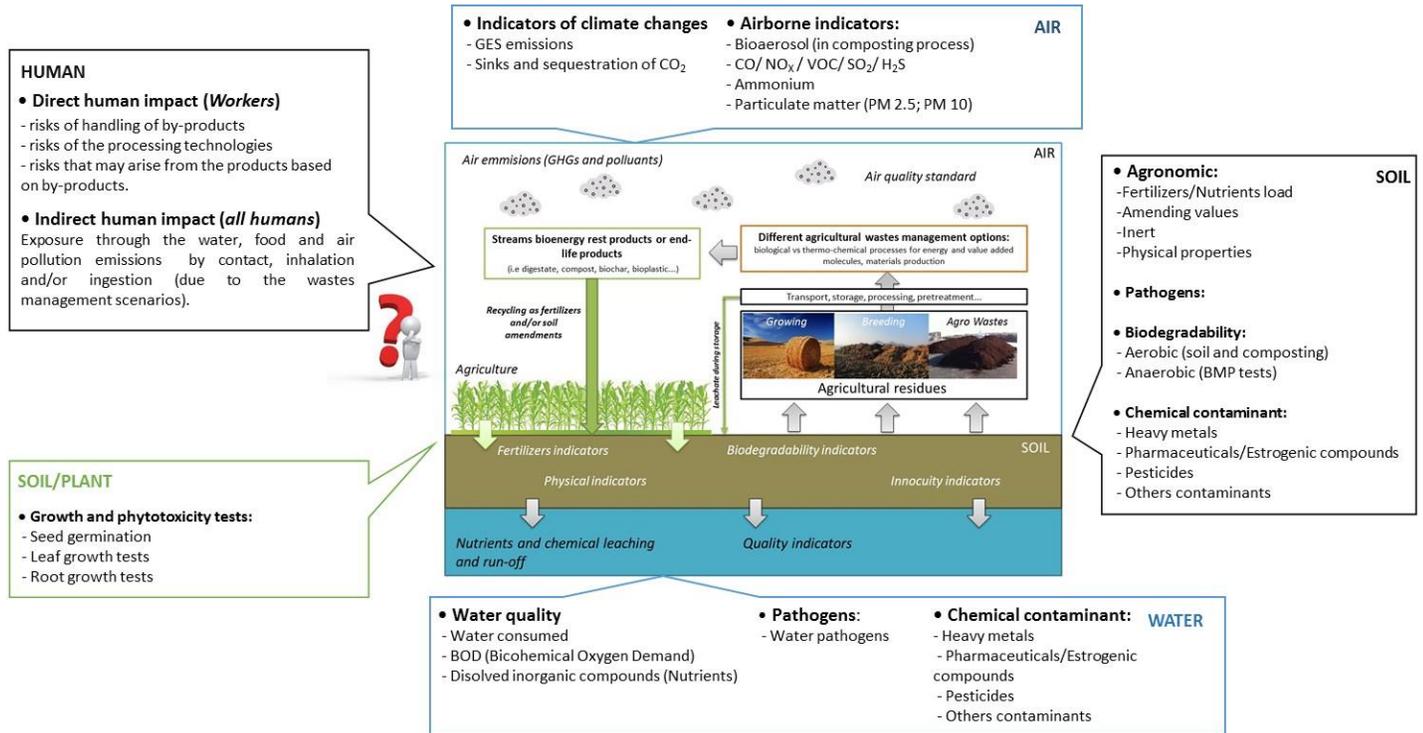


Fig. 6. Summarize of the various sustainability indicators (i.e. environmental and human) that have been defined for the NoAW project.

- The methodologies that will be used during the project have also been described. These methodologies will be further implemented by the various partners of the WP3 and WP (experimental core of the project)
- These lists of indicators have been defined according literature data and stakeholders partners but at this stage, the list is probably not complete and will be incremented all over the NoAW project. This remark is even truer for the human indicators as most of innovative processes are still under laboratory scale and it is thus difficult to identify clearly the human impact. Probably, up-scaling at pilot industrial scale will be necessary to assess more precisely the environmental and human indicators.
- Interestingly, it has been shown that for most of organic residues uses in land application, no consensus exist in term of European legislation and guidelines or threshold limits are differently established at National Level, partially due to differences in soil legislation. This lack of harmonization creates legal uncertainties for wastes management decisions. For some emergent contaminant (i.e. veterinary, estrogens, antibiotic...) there is clearly absence of legislation and in most cases even at the National level. For sure, a harmonization in European countries along with assessment of adapted Norm for quantified these indicators will help in improving stakeholders and consumers' confidence, promoting the trade of agricultural by-products.

These indicators will be further used in different tasks of the project to implement the sustainability of the various processes by:

- Serving as base for the Life Cycle Assessment (LCA) Analysis in **WP2**.
- Be used in the stakeholder’s surveys that will be implemented in task 1.3 for investigating and mapping economic, environmental and social challenges and opportunities of agro-waste chains.
- Implementing the multi-criteria sensitive analysis tools developed in **WP2**.
- Serving to evaluate the overall sustainability of the various wastes management processes in combination with economical and other social indicators.

Finally, for most of the indicators developed, some preliminary insights have been provided regarding European legislation (harmonized or for each European countries) and threshold level. These legislation aspect will be discussed more in depth in the **task 1.3**.

7. Partners involved in the work

The following partner described in the Table X have been involved in the realization of the deliverable 1.1. Some surveys have also been lead with all the partners of the WP3 and WP4 of the NoAW project.

In summarize:

- APESA (Association pour l’Environnement et la Sécurité en Aquitaine) have been in charge of agronomic indicators and soil/plant indicators. APESA as task leader have also been responsible of the draft harmonization.
- UNIROMA have been in charge of chemical contaminants indicators in both soil and water bodies.
- VERMI have been in charge of pathogens and water quality indicators
- UM (Université de Montpellier) have been in charge of indicators of bioplastics biodegradability in compost, anaerobic digestion and soil.
- CBHU have been in charge of the human and safety risks indicators.

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Table 7. Partners involved in the task 1.5 and the deliverable 1.1.

Note 4: From the initial sharing of the **Fig.3**, it is important to notice that SYSU partner due to the absence of financial support from Chinese countries have not participated on time. Work on AIR indicators have been partially assumed by APESA partner.

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