Soluble Biobased Substances

Subjects: Green & Sustainable Science & Technology
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Soluble bio-based substances (SBS) may be isolated from the anaerobic digestate of the organic humid fraction of urban waste; from the whole vegetable compost made from gardening residues and from the compost obtained after aerobic digestion of a mixture of urban waste digestate, gardening residues and sewage sludge.

Keywords: bio-based substances ; biostimulants ; digestate ; compost

1. Introduction

Cultivating plants is a human activity involving several sectors. Agriculture deals with cultivation of crops for human consumption as well as animal production. Horticulture strictly involves the cultivation of plants for food consumption, as well as plants not for human consumption. Horticulture differs from floriculture. The former involves different types of garden crops, while the latter involves flowering and foliage plants. Ornamental horticulture is the cultivation of decorative plants of all kinds, including not only plants with attractive flowers, but also plants with decorative leaves, stems, bark, or fruit. Basically, floriculture and ornamental horticulture have decorative and aesthetic purposes. Aside from categories' definitions and differences in the cultivated species, all these categories' activities share similar problems.

Common farming practice is to boost plant production with a fertilizer dose higher than that adsorbed by soil and plant. Thus, noxious fertilizers' components accumulate in soil, reach the food chain, leach through soil into ground water, and ultimately affect human and animal health. Mineral and organic fertilizers are used. The global fertilizer market is 156 billion USD/year. [1]. Major ones are urea and mineral phosphates (80% of the EU fertilizers' market value), with 0.11–0.46 €/kg production cost. They are based on energy-intensive production processes or manufactured from non-renewable feedstock imported from third countries [2]. Organic fertilizers belong to a niche market (0.15% of the total fertilizer market) [3]. The world consumption of mineral fertilizers containing N, P and K is ca. 200 Mt/year [4]. EU consumption of mineral fertilizers is 16 Mt/year [5]. From 70 to 250 kg/ha nitrates leaching may occur depending on fertilizer dose, soil, and plant type [6]. Based on average 51 kg/ha applied surplus and total 175 Mha cultivated area, 9 kt/year nitrate leach through soil and water. To improve the balance between fertilizers dose and crop requirement, the max EU ruled dose is 150–350 kg/ha. Major organic fertilizers are composts of biowastes from urban, animal, or agriculture sources, manure, peat and leonardite hydrolysates. Composts are commonly applied to soil at 10–30 t/ha.year [7]. High doses that obtain the desired effects are due to compost insolubility causing slow nutrients' uptake by plants. This causes leaching of excess major and trace metal components through soil and water. Similarly, manure is applied at 70 t/ha dose. In addition to leaching, manure causes greenhouse-gases emission due to fermentation in soil. For example, typical aerial NH_3 concentration in a pig farm is 5–35 ppm against a 25 ppm threshold level [8]. A higher NH_3 level harms both animal and human health. Emission of 420,000 t/year NH_3 is estimated from a total 1400 Mt/year EU manure production [9]. Peat and leonardite hydrolysates contain soluble organic and mineral matter. EU consumption is 240 kt/year. These hydrolysates are obtained from fossil source. Based on average 40% C content, their use causes 355 kt/year CO_2 emission from fossil C and depletion of fossil sources. Except for municipal biowastes (MBW), a common problem of all fertilizers is that their sources are found in restricted sites, not available worldwide. This poses the problem of product supply and cost. The problem is highly relevant in Europe, which imports most of its mineral consumption from third countries.

One other important restraint on plant productivity is pests and diseases. These are highly relevant for food plants. Food production loss due to plant diseases is estimated to be 10–50%/year [10]. Plant protection relies on pesticides use, which increases food cost and may cause hormonal disruption in human. A common problem of all fertilizers is the need to use them together with pesticides. Together with lowering cost, there is much concern for decreasing the exploitation and depletion of natural resources to produce fertilizers.

2. SBS Composition and Properties

The soluble bioorganic substances (SBS) are obtained by hydrolysis at 60–90 °C and pH 13 of several different mixes of urban food, green and sewage sludge wastes fermented under anaerobic and aerobic conditions [11]. Under these conditions, the SBS were obtained together with the secondary insoluble (IR) product. The fermented wastes yielding the SBS described in here were sampled from different streams of the Italian ACEA Pinerolese MBW treatment plant. The SBS contain organic and mineral matter. The organic matter is a mix of molecules with molecular weight from 5 to over 750 kDa. These molecules are constituted by several different organic moieties made by aliphatic and aromatic C substituted by acid and basic functional groups of different strengths. Mineral elements of groups 1 to 4 are bonded to or complexed by the organic moieties. These chemical features are inherited from the pristine biowastes. The molecules contained in SBS are water soluble memories of the native recalcitrant lignocellulosic polysaccharides, proteins, fats, and lignin proximates still present in the biowastes after anaerobic and aerobic fermentation. It is no wonder that, due to their origin, richness of mineral elements, organic functional groups and acquired water solubility, the SBS molecules exhibit a wide range of properties as plant biostimulants, plant resistance inducers, bio-photosensitizers, oxidation catalysts, polymers for manufacturing mulch films, composite pellets, composite plastic articles, and high performance surfactants. **Table 1**, **Table 2**, **Table 3** and **Table 4** report the compositional details of the SBS, IR and the pristine fermented biowastes. **Table 5** list the plants cultivated with the SBS and summarizes the main SBS effects on the cultivated plants. All data in **Table 1**, **Table 2**, **Table 3**, **Table 4** and **Table 5** are extrapolated from the references cited in **Table 5**. The data reported in **Table 1**, **Table 2**, **Table 3** and **Table 4** were obtained through a specifically designed analytical protocol [11]. This included calculation of moisture, ash and volatile solids (VS) contents from the sample weight losses determined after heating to 105 and 650 °C, inorganic elements analysis by AAS and/or ICP, microanalyses for C, H, N determination performed with a C. Erba (Rodano, Milan, Italy) NA-2100 elemental analyser. The C types and functional groups reported in **Table 4** were determined by solid-state 13C NMR spectroscopy. Solid-state 13C NMR spectra were acquired at 67.9 MHz on a JEOL GSE 270 spectrometer equipped with a Doty probe. The cross-polarization magic angle spinning (CPMAS) technique was employed, and for each spectrum, about 104 free induction decays were accumulated. The pulse repetition rate was set at 0.5 s, the contact time at 1 ms, the sweep width was 35 KHz, and MAS was performed at 5 kHz. Signals assignment as a function of the resonance range were: 0–53 ppm aliphatic C, 53–63 ppm O-Me or N-alkyl C, 63–95 ppm O-alkyl C, 95–110 ppm di-O-alkyl C, 110–140 ppm aromatic C, 140–160 ppm phenol or phenyl ether C, 160–185 ppm carboxyl C, and 185–215 ppm ketone C.

Table 1. Waste ingredients in pristine biowastes (PFB).

PFB	Ingredients
D	Digestate from anaerobic fermentation of unsorted food wastes
CV	Compost of private gardening and public park trimming residues (V)
CVD	Compost of D and V mix in 2/1 weight respective ratio
CVDF	Compost of D, V and sewage sludge (F) mix in 5.5/3.5/1 respective ratio
ETP	Exhausted tomato plants at the end of the crop harvesting season

Table 2. Mineral elements and ash content (*w/w*%) in the pristine biowastes (PFB), in the soluble (SBS) product and insoluble (IR) hydrolysates obtained.

	Si	Fe	Al	Mg	Ca	K	Na	Ash
CVDF PFB	6.27 ± 0.04	1.02 ± 0.01	1.06 ± 0.02	0.83 ± 0.01	3.23 ± 0.05	1.32 ± 0.03	0.07 ± 0.01	59.4
CVDF SBS	0.92 ± 0.03	0.53 ± 0.02	0.44 ± 0.02	0.49 ± 0.01	2.59 ± 0.03	5.49 ± 0.04	0.15 ± 0.01	27.3
CVDF IR	7.68 ± 0.06	1.23 ± 0.03	1.05 ± 0.01	1.15 ± 0.02	3.20 ± 0.03	1.32 ± 0.02	0.04 ± 0.01	77.6
D PFB	3.46 ± 0.05	0.77 ± 0.03	0.40 ± 0.02	0.88 ± 0.02	7.16 ± 0.08	0.53 ± 0.03	0.22 ± 0.02	34.5
D SBS	0.36 ± 0.03	0.16 ± 0.00	0.78 ± 0.04	0.18 ± 0.01	1.32 ± 0.05	9.15 ± 0.06	0.39 ± 0.01	15.4
D IR	4.73 ± 0.03	0.48 ± 0.01	0.47 ± 0.06	1.07 ± 0.02	9.54 ± 0.05	3.44 ± 0.05	0.16 ± 0.01	49.0
CVD PFB	10.70 ± 0.03	1.07 ± 0.02	0.71 ± 0.03	1.12 ± 0.01	4.27 ± 0.14	1.09 ± 0.03	0.08 ± 0.01	56.1
CVD SBS	2.49 ± 0.04	0.88 ± 0.02	0.60 ± 0.06	0.93 ± 0.02	4.70 ± 0.08	3.76 ± 0.07	0.17 ± 0.01	28.3

	Si	Fe	Al	Mg	Ca	K	Na	Ash
CVD IR	**12.60 ± 0.05**	**0.95 ± 0.01**	**0.75 ± 0.03**	**1.13 ± 0.02**	**4.96 ± 0.05**	**2.13 ± 0.06**	**0.07 ± 0.01**	**56.8**
CV PFB	**12.14 ± 0.07**	**1.03 ± 0.02**	**0.59 ± 0.01**	**1.67 ± 0.25**	**4.86 ± 0.61**	**1.18 ± 0.07**	**0.06 ± 0.01**	**57.1**
CV SBS	**2.55 ± 0.01**	**0.77 ± 0.04**	**0.49 ± 0.04**	**1.13 ± 0.06**	**6.07 ± 0.38**	**3.59 ± 0.21**	**0.16 ± 0.01**	**27.9**
CV IR	**15.04 ± 0.33**	**1.10 ± 0.05**	**0.67 ± 0.01**	**1.45 ± 0.01**	**4.19 ± 0.09**	**1.49 ± 0.02**	**0.06 ± 0.01**	**71.3**
ETP PFB	**0.98 ± 0.03**	**0.30 ± 0.02**	**0.27 ± 0.02**	**0.42 ± 0.02**	**4.65 ± 0.03**	**3.30 ± 0.02**	**0.22 ± 0.01**	**20.2**
ETP SBS	**0.22 ± 0.03**	**0.33 ± 0.02**	**0.34 ± 0.03**	**0.80 ± 0.04**	**2.10 ± 0.02**	**9.15 ± 0.06**	**0.24 ± 0.01**	**23.3**
ETP IR	**0.85 ± 0.03**	**0.25 ± 0.01**	**0.17 ± 0.01**	**0.27 ± 0.01**	**4.41 ± 0.02**	**4.49 ± 0.06**	**0.15 ± 0.01**	**36.9**

Table 3. Total C, N and P content (*w/w*%) in pristine biowastes (PFB), and in soluble (SBS) and insoluble (IR) hydrolysates obtained.

	C	N	C/N	P_2O_5
CVDF PFB	**24.36 ± 0.16**	**2.25 ± 0.11**	**10.83**	**1.30 ± 0.22**
CVDF SBS	**35.47 ± 0.09**	**4.34 ± 0.17**	**8.17**	**1.44 ± 0.03**
CVDF IR	**11.72 ± 0.22**	**1.02 ± 0.05**	**11.49**	**0.53 ± 0.05**
D PFB	**29.99 ± 0.20**	**3.81 ± 0.12**	**7.87**	**3.27 ± 0.15**
D SBS	**45.07 ± 0.12**	**7.87 ± 0.12**	**5.73**	**1.14 ± 0.10**
D IR	**27.68 ± 0.08**	**1.80 ± 0.05**	**15.38**	**2.75 ± 0.03**
CVD PFB	**27.07 ± 0.78**	**2.45 ± 0.07**	**11.05**	**0.75 ± 0.05**
CVD SBS	**37.51 ± 0.04**	**4.89 ± 0.03**	**7.67**	**0.84 ± 0.04**
CVD IR	**22.11 ± 0.24**	**1.64 ± 0.01**	**13.48**	**1.14 ± 0.18**
CV PFB	**22.43 ± 0.42**	**1.91 ± 0.03**	**11.74**	**0.39 ± 0.02**
CV SBS	**38.25 ± 0.09**	**4.01 ± 0.03**	**9.54**	**0.53 ± 0.05**
CV IR	**18.44 ± 0.67**	**1.15 ± 0.09**	**16.03**	**0.37 ± 0.02**
ETP PFB	**36.44 ± 0.24**	**3.51 ± 0.18**	**10.38**	
ETP SBS	**47.30 ± 0.09**	**6.52 ± 0.13**	**7.25**	
ETP IR	**28.83 ± 0.08**	**2.52 ± 0.10**	**11.44**	

Table 4. Carbon types and functional groups content (*w/w*% of total C) [a].

	Cal	OMe + NR	OR	OCO	Ph	PhOY	COX	CO
CVDF PFB	**31.81**	**8.59**	**27.67**	**6.18**	**10.72**	**5.90**	**8.17**	**1.96**
CVDF SBS	**31.17**	**7.88**	**19.13**	**6.73**	**16.58**	**7.69**	**10.49**	**0.34**
CVDF IR	**28.90**	**8.32**	**27.14**	**7.46**	**13.23**	**7.01**	**6.79**	**1.16**
D PFB	**33.60**	**9.10**	**26.61**	**5.99**	**8.94**	**4.27**	**10.53**	**0.97**
D SBS	**43.38**	**9.86**	**14.01**	**3.37**	**9.60**	**3.23**	**15.89**	**0.66**
D IR	**50.80**	**5.52**	**18.95**	**4.00**	**8.54**	**3.28**	**7.23**	**1.68**
CVD PFB	**37.25**	**9.75**	**28.14**	**4.35**	**8.03**	**5.20**	**6.67**	**0.62**
CVD SBS	**40.90**	**7.34**	**14.18**	**3.85**	**12.27**	**5.97**	**12.92**	**2.56**
CVD IR	**31.73**	**9.39**	**29.32**	**6.39**	**9.78**	**6.21**	**5.87**	**1.31**
CV PFB	**32.86**	**8.33**	**23.85**	**6.34**	**12.30**	**6.73**	**8.21**	**1.37**
CV SBS	**36.90**	**7.24**	**13.22**	**4.18**	**13.39**	**6.84**	**13.53**	**4.69**

	Cal	OMe + NR	OR	OCO	Ph	PhOY	COX	CO
CV IR	**31.70**	**8.43**	**24.58**	**6.14**	**11.49**	**7.23**	**7.74**	**2.68**
ETP PFB	**14.34**	**7.22**	**49.60**	**11.62**	**6.89**	**3.44**	**6.28**	**0.61**
ETP SBS	**47.38**	**9.39**	**10.39**	**2.19**	**11.50**	**3.81**	**14.37**	**0.97**
ETP IR	**5.00**	**7.97**	**58.98**	**13.19**	**7.00**	**3.66**	**2.97**	**1.22**

[a] Aliphatic (Cal), aromatic (Ph), anomeric (OCO), carboxylic and/or amide (COX), ketone (CO) carbon, and carbon bonded to amine (NR), methoxy (OMe), alkoxy (OR), and phenolic and/or phenoxy (PhOY) groups.

Table 5. Plants cultivated with SBS and SBS effects: increase (*w/w*% relative to control) of total biomass or crop production, unless otherwise indicated.

	CVDF	CVD	CV	D	ETP
Euphorbia [12]	**331**			**117**	
Lantana [13]	**143**			**85**	
Hibiscus [14][15] [a]			**15**	**23**	
Murraya [16]	**67**			**35**	
Tomato Micro-Tom [17] [b]					
***Tomato Lycopersicon* [7][18] [c]**	**16**	**4–13**	**21**	**5**	
Tomato Micro-Tom [19]	**46**		**1**	**16**	
Red pepper [20]		**66**			
Maize [21]	**89**				
Bean [22]					**109–1750 [d,e]**
Grain [19]	**10**		**9**	**9**	
Tobacco [19]	**6**		**0**	**0**	
Spinach [23]				**24–40 [f]**	
Oilseed Rape [10]	**56 [g]**			**42 [g]**	

[a] Reference 13 for CV and 17 for D. [b] Used only as model plant. [c] Reference 20 for CVD and 21 for CVDF, CV and D. [d] Increase of enzyme activities and soluble proteins concentration in leaves and roots. [e] Increase of root diameter (66%) by ETP PFB, SBS and IR, and of chlorophyll b (135%) by ETP SBS and IR. [f] Reduction of nitric to total N ratio in leaves. [g] Reduction of plant lesions due to Leptosphaeria maculans.

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