Title: Pyrolysis of municipal sewage sludge: challenges, opportunities and new valorization routes for biochar, bio-oil, and pyrolysis gas.

Authors: Vincenzo Pelagalli [a], Michela Langone [b], Silvio Matassa [c], Marco Race [a], Riccardo Tuffi [d], Stefano Papirio [c], Piet N.L. Lens [e], Marco Lazzazzara [f], Alessandro Frugis [f], Luigi Petta [g], Giovanni Esposito [c]

[a] Department of Civil and Mechanical Engineering, University of Cassino and Southern Lazio, Via Di Biasio 43, 03043 Cassino, Italy. (E-mail: vincenzo.pelagalli@unicas.it; marco.race@unicas.it).

[b] Laboratory Technologies for the Efficient Use and Management of Water and Wastewater, Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA), Via Anguillarese, 301, 00123 Rome, Italy. (E-mail: michela.langone@ENEA.it).

[c] Department of Civil, Architectural and Environmental Engineering, University of Napoli Federico II, Via Claudio 21, 80125 Napoli, Italy. (E-mail: silvio.matassa@unina.it; stefano.papirio@unina.it; gioespos@unina.it).

[d] Laboratory Technologies for the Reuse, Recycling, Recovery and valorization of Waste and Materials, Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA), Via Anguillarese, 301, 00123 Rome, Italy. (E-mail: riccardo.tuffi@ENEA.it).

[e] National University of Ireland, Galway, University Road, Galway, H91 TK33, Ireland.

(E-mail: piet.lens@universityofgalway.ie).

[f] ACEA ELABORI SpA, Via Vitorchiano 165, Rome, Italy. (E-mail: marco.lazzazzara@aceaspa.it; alessadro.frugis@aceaspa.it).

[g] Laboratory Technologies for the Efficient Use and Management of Water and Wastewater, Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA), Via Martiri di Monte Sole, 4, 40129 Bologna, Italy. (E-mail: luigi.petta@ENEA.it).

Corresponding author: Vincenzo Pelagalli (E-mail: vincenzo.pelagalli@unicas.it)

Supplementary material

A. European legislation on municipal sewage sludge management

To establish more sustainable municipal sewage sludge (MSS) management practices, extensive legislation was produced by the European Commission. MSS is classified as a "non-hazardous" solid waste [1]. Several directives from the European Union such as the Water Framework Directive [2] and the Waste Framework Directive [3] influence MSS management by establishing a hierarchical approach foreseeing waste prevention (*e.g.* minimization techniques), preparation for reuse (*e.g.* chemical or biological stabilization), recycling (*e.g.* material recovery), other recovery (*e.g.* energy recovery), and disposal (*e.g.* landfilling) [4].

The implementation of the Council Directive 91/271/EEC [5] concerning urban wastewater treatment, also known as "Urban Waste Water Treatment Directive" (UWWTD), has affected the increase in the amount of generated MSS. However, the Directive encourages the valorization of MSS whenever appropriate and regulates its use in order to minimize hazardous effects on the environment; thus, it

was determinant for adapting to other disposal and treatment methods beyond the landfill. Subsequently, the Council Directive 91/676/EEC [6], concerning water protection against pollution caused by nitrates from agricultural sources, resulted in a reduction of areas on which MSS can be used for agricultural purposes. Council Directive 1999/31/EEC [7] introduced stringent new standards related to landfilling of biodegradable waste, while Directive 2018/850 [8] amended the former by extending such limitations to "*waste that is suitable for recycling or other recovery*", therefore including MSS.

Generally, MSS recovery methods can be categorized under two different management routes: an organic recycling route (including agricultural spreading and composting) and a route focused on the recovery of energy and materials (including thermochemical conversion methods) [9]. In order to align the Directive with the ambitions reported in the European Green Deal and the Zero Pollution Action Plan, the European Commission opened in 2020 a public consultation for the revision of the UWWTD [10], including new circular approaches to MSS management for the recovery of nutrients, materials and energy, as well as the importance of MSS usage as fertilizer.

The most meaningful document concerning the organic recycling route is the Council Directive 1986/278/EEC [11], also known as "Sewage Sludge Directive" (SSD), which is aimed at regulating the use of MSS in agriculture. On the other hand, toxic organic and inorganic pollutants contained within MSS could be highly dangerous if dispersed in the environment because of their persistence and possible toxicity to people and wildlife [12–16]. By defining specific limits on potentially toxic elements (PTEs) concentration both in treated MSS and soils on which MSS is distributed, the SSD aimed at preventing harmful effects on soil, vegetation, animals and humans. To this end, it also prohibits the use of untreated MSS on agricultural land unless it is injected or incorporated into the soil. The SSD did not introduce limits on organic pollutants concentration nor on the presence of pathogens in soils. Therefore, to mitigate the environmental risks associated with the agricultural reuse of MSS, many EU Member States have established their own legislation to regulate these substances within MSS and/or soils, further setting more stringent limits for PTEs [17]. Lately, in light of the most recent environmental strategies and planning tools such as the New Circular Economy Action Plan [18], the European Green Deal [19], the Bioeconomy Strategy [20], the Farm to Fork Strategy [21], the EU Biodiversity Strategy for 2030 [22], and the post-Covid-19 recovery plan for Europe [23], the Directive has gained additional significance and a process of revision is currently ongoing [24], in order to exploit the potential of MSS in the context of the circular economy transition, in order to contribute to increasing resource efficiency and protect human health. A first result of this revision process has been the new Regulation 2019/1009 [25] on the market of fertilizing products, introducing for the first

time organic and, in particular, bio-based and recovered fertilizers beyond mineral/inorganic ones as fertilizing products, aiming to harmonize their production and composition. Due to their micropollutant content, "pyrolysis and gasification materials" (including biochar) derived from MSS have been excluded from the EU fertilizing products [26].

Regarding the material recycling route, many valuable raw materials can be recovered from MSS: water, compost, nutrients, agronomic additives, sulfur, phosphorous salts, fibers, proteins, biomass, up to more complex materials such as biopolymers [27–32]. However, in accordance with the Waste Framework Directive, most of these materials are classified as waste when obtained from MSS. Nevertheless, the new Fertilising Products Regulation [25], applied from July 2022, already defined conditions to obtain an "End-of-Waste" status for struvite and ash-based products from MSS. In order to develop a real market for such secondary materials, additional criteria should be proposed and discussed at the EU level in the near future.

Finally, concerning the energy recovery route, the EU aims to the following main waste-to-energy processes: incineration, AD, production of waste-derived solid, liquid or gaseous fuels, and other thermal treatments such as pyrolysis or gasification [33]. With this scope, Directive 2009/28/EC [34] (subsequently modified to the currently in-force Directive 2018/2001 [35]) promoted the use of energy from renewable sources, recognizing energy derived from biomass, landfills, and WWTP as a renewable energy source.

References

1 European Commission, Commission Decision of 3 May 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste (notified under document number C(2000) 1147) (Text with EEA relevance), 2000, http://data.europa.eu/eli/dec/2000/532/oj, (accessed 07 April 2024).

2 European Commision, Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy, 2000, http://data.europa.eu/eli/dir/2000/60/oj, (accessed 07 April 2024).

3 European Parliament and Council, Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives (Text with EEA relevance), http://data.europa.eu/eli/dir/2008/98/oj, (accessed 24 January 2024).

4 M. C. Collivignarelli, A. Abbà, A. Frattarola, M. C. Miino, S. Padovani, I. Katsoyiannis and V. Torretta, sustainability Legislation for the Reuse of Biosolids on Agricultural Land in Europe: Overview, , DOI:10.3390/su11216015.

5 Council of the European Communities, COUNCIL DIRECTIVE of 21 May 1991 concerning urban waste water treatment (91/271/EEC), 1991, http://data.europa.eu/eli/dir/1991/271/oj, (accessed 07 April 2024).

6 Council of the European Communities, Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources, 1991, http://data.europa.eu/eli/dir/1991/676/oj, (accessed 07 April 2024).

7 European Commission, COUNCIL DIRECTIVE 1999/31/EC of 26 April 1999 on the landfill of waste, 1999, http://data.europa.eu/eli/dir/1999/31/oj, (accessed 07 April 2024).

8 European Parliament and Council, Directive (EU) 2018/850 of the European Parliament and of the Council of 30 May 2018 amending Directive 1999/31/EC on the landfill of waste (Text with EEA relevance), http://data.europa.eu/eli/dir/2018/850/oj, (accessed 24 January 2024).

9 M. Kacprzak, E. Neczaj, K. Fijałkowski, A. Grobelak, A. Grosser, M. Worwag, A. Rorat, H. Brattebo, Å. Almås and B. R. Singh, Sewage sludge disposal strategies for sustainable development, Environ Res, 2017, 156, 39–46.

10 European Commission, Proposal for a DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL concerning urban wastewater treatment (recast).

11 Council Directive 86/278/EEC, Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture, Official Journal L 181 , 04/07/1986 P. 0006 - 0012.

12 C. Li, N. Le-Minh, J. A. McDonald, A. S. Kinsela, R. M. Fisher, D. Liu and R. M. Stuetz, Occurrence and risk assessment of trace organic contaminants and metals in anaerobically co-digested sludge, Science of The Total Environment, 2022, 816, 151533.

13 M. D. Hatinoğlu and F. D. Sanin, Sewage sludge as a source of microplastics in the environment: A review of occurrence and fate during sludge treatment, J Environ Manage, 2021, 295, 113028.

14 L. Lamastra, N. A. Suciu and M. Trevisan, Sewage sludge for sustainable agriculture: Contaminants' contents and potential use as fertilizer, Chemical and Biological Technologies in Agriculture, , DOI:10.1186/s40538-018-0122-3.

15 M. Langone, G. Sabia, L. Petta, L. Zanetti, P. Leoni and D. Basso, Evaluation of the aerobic biodegradability of process water produced by hydrothermal carbonization and inhibition effects on the heterotrophic biomass of an activated sludge system, J Environ Manage, 2021, 299, 113561.

16 F. Corradini, P. Meza, R. Eguiluz, F. Casado, E. Huerta-Lwanga and V. Geissen, Evidence of microplastic accumulation in agricultural soils from sewage sludge disposal, Science of The Total Environment, 2019, 671, 411–420.

17 G. Mininni, A. R. Blanch, F. Lucena and S. Berselli, EU policy on sewage sludge utilization and perspectives on new approaches of sludge management, Environmental Science and Pollution Research, , DOI:10.1007/s11356-014-3132-0.

18 European Commission, Communication from the Commission: A new Circular Economy Action Plan For a cleaner and more competitive Europe, https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:52020DC0098, (accessed 1 June 2023).

19 European Commission, Communication from the Commission: The European Green Deal, 2019, https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:52019DC0640, (accessed 1 June 2023).

20 European Commission, A sustainable bioeconomy for Europe – Strengthening the connection between economy, society and the environment : updated bioeconomy strateg, 2018, https://data.europa.eu/doi/10.2777/792130, (accessed 1 June 2023).

21 European Commission, Communication from the Commission: A Farm to Fork Strategy, https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:52020DC0381, (accessed 1 June 2023).

22 European Commission, EU biodiversity strategy for 2030 – Bringing nature back into our lives, 2021, https://data.europa.eu/doi/10.2779/677548, (accessed 1 June 2023).

23 European Commission, The EU's 2021-2027 long-term budget and NextGenerationEU – Facts and figures, 2021, https://data.europa.eu/doi/10.2761/808559, (accessed 1 June 2023).

24 European Commission, Sewage sludge use in farming: evaluation, https://ec.europa.eu/info/law/better-regulation/have-your-say/initiatives/12328-Sewage-sludge-use-in-farming-evaluation_en, (accessed 1 June 2023).

25 European Parliament and Council, Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003 (Text with EEA relevance), 2019, http://data.europa.eu/eli/reg/2019/1009/oj, (accessed 03 June 2023).

26 European Commission, 2021, ANNEXES to the Commission Delegated Regulation amending Annexes II, III and IV to Regulation (EU) 2019/1009 of the European Parliament and of the Council for the purpose of adding pyrolysis or gasification materials as a component material category in EU fertilising products, https://ec.europa.eu/info/law/better-regulation/have-your-say/initiatives/12136-Fertilising-products-pyrolysis-and-gasification-materials_en, (accessed 02/02/2022)

27 M. Hu, H. Hu, Z. Ye, S. Tan, K. Yin, Z. Chen, D. Guo, H. Rong, J. Wang, Z. Pan and Z. T. Hu, A review on turning sewage sludge to value-added energy and materials via thermochemical conversion towards carbon neutrality, J Clean Prod, 2022, 379, 134657.

28 L. Isern-Cazorla, A. Mineo, M. E. Suárez-Ojeda and G. Mannina, Effect of organic loading rate on the production of Polyhydroxyalkanoates from sewage sludge, J Environ Manage, 2023, 343, 118272.

29 M. Hušek, J. Moško and M. Pohořelý, Sewage sludge treatment methods and P-recovery possibilities: Current state-of-the-art, J Environ Manage, 2022, 315, 115090.

30 S. Vilakazi, E. Onyari, O. Nkwonta and J. K. Bwapwa, Reuse of domestic sewage sludge to achieve a zero waste strategy & improve concrete strength & durability - A review, S Afr J Chem Eng, 2023, 43, 122–127.

31 K. Chojnacka, D. Skrzypczak, D. Szopa, G. Izydorczyk, K. Moustakas and A. Witek-Krowiak, Management of biological sewage sludge: Fertilizer nitrogen recovery as the solution to fertilizer crisis, J Environ Manage, 2023, 326, 116602.

32 A. Raheem, V. S. Sikarwar, J. He, W. Dastyar, D. D. Dionysiou, W. Wang and M. Zhao, Chemical Engineering Journal, 2018, 337, 616–641.

33 European Commission, Communication from the Commission to the European Parliament, the Council, the European economic and social committee and the Committee of the regions: The role of waste-to-energy in the circular economy, 2017, https://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:52017DC0034, (accessed 07 April 2024).

34 European Parliament and Council, Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC, 2009, http://data.europa.eu/eli/dir/2009/28/oj.

35 European Parliament and Council, DIRECTIVE (EU) 2018/2001 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 11 December 2018 on the promotion of the use of energy from renewable sources, 2018, http://data.europa.eu/eli/dir/2018/2001/2023-11-20, (accessed 07 April 2024).