Crop production and analysis of quality and safety in different cultivation and climatic conditions

This work is aimed at understanding if the use of biochar in agriculture is a safe practice for human health. Thirty-four organic micropollutants of the classes of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and nitro-PAHs (NPAHs) were analyzed in five samples tomatoes, grown up with different biochar % and irrigated with fresh water, trials.

All the tomato sample trials grown up at the Project Coordinator unit, irrigated with the same amount of fresh water (201,56 L for each plant) at the outdoor laboratory of the Department of Chemistry of the University of Florence. The fruits then were cut into slides and dried 48 hours at 60°C in oven. Once dried, they were ground with a mortar to obtain sample homogeneity and finally stored at -18°C until they were analyzed at Department of Chemistry of the University of Turin.

- BC0: base substrate (peat) 100%
- BC5: base substrate 95% + 5% biochar v/v
- BC10: base substrate 90% + 10% biochar v/v
- BC20: base substrate 80% + 20% biochar v/v
- BC40: base substrate 60% + 40% biochar v/v

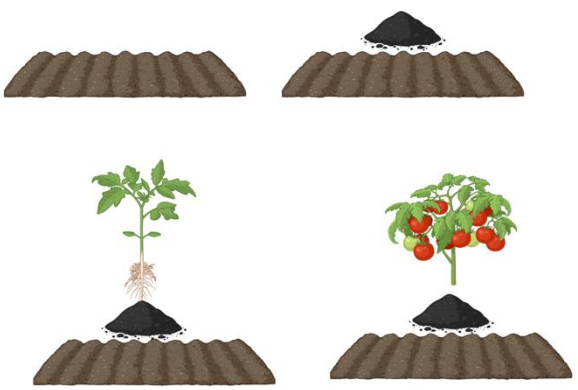

Figure 1 – Grown of tomatoes plant with biochar

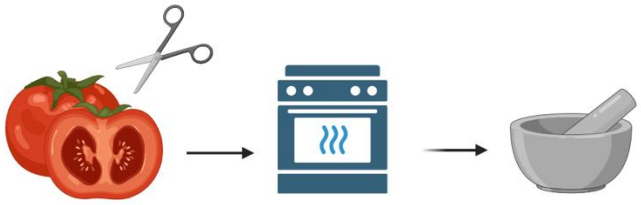

Figure 2 – Treatment of grown tomatoes

FOSC
ERA-NET Cofund on Food Systems and Climate

This project has received funding from the European Union's Horizon 2020 research and Innovation programme under grant agreement No 862555

For the determination of organic pollutants QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) procedure has been used. This is an innovative methodology employed for the preparation of complex samples, such food, for the analysis of pesticide residues and contaminants. Here are its key principles:

- Quick: The QuEChERS procedure is designed to be fast and efficient, allowing for the rapid preparation of many samples in a short amount of time.
- Easy: The methodology is intended to be accessible and user-friendly, reducing the complexity of the sample preparation process.
- Cheap: QuEChERS is a cost-effective method, requiring less time, fewer solvents and fewer resources compared to other techniques.
- Effective: Despite its simplicity and convenience, the QuEChERS procedure is highly effective in extracting a wide range of analytes.
- Rugged: its robustness allows successful application to a variety of samples and analytical conditions without compromising the quality of results.
- Safe: The procedure is designed to ensure operator safety and compliance, limiting the use of hazardous and harmful substances.

In summary, QuEChERS procedure represents a modern approach providing reliable results in the analysis of food contaminants.

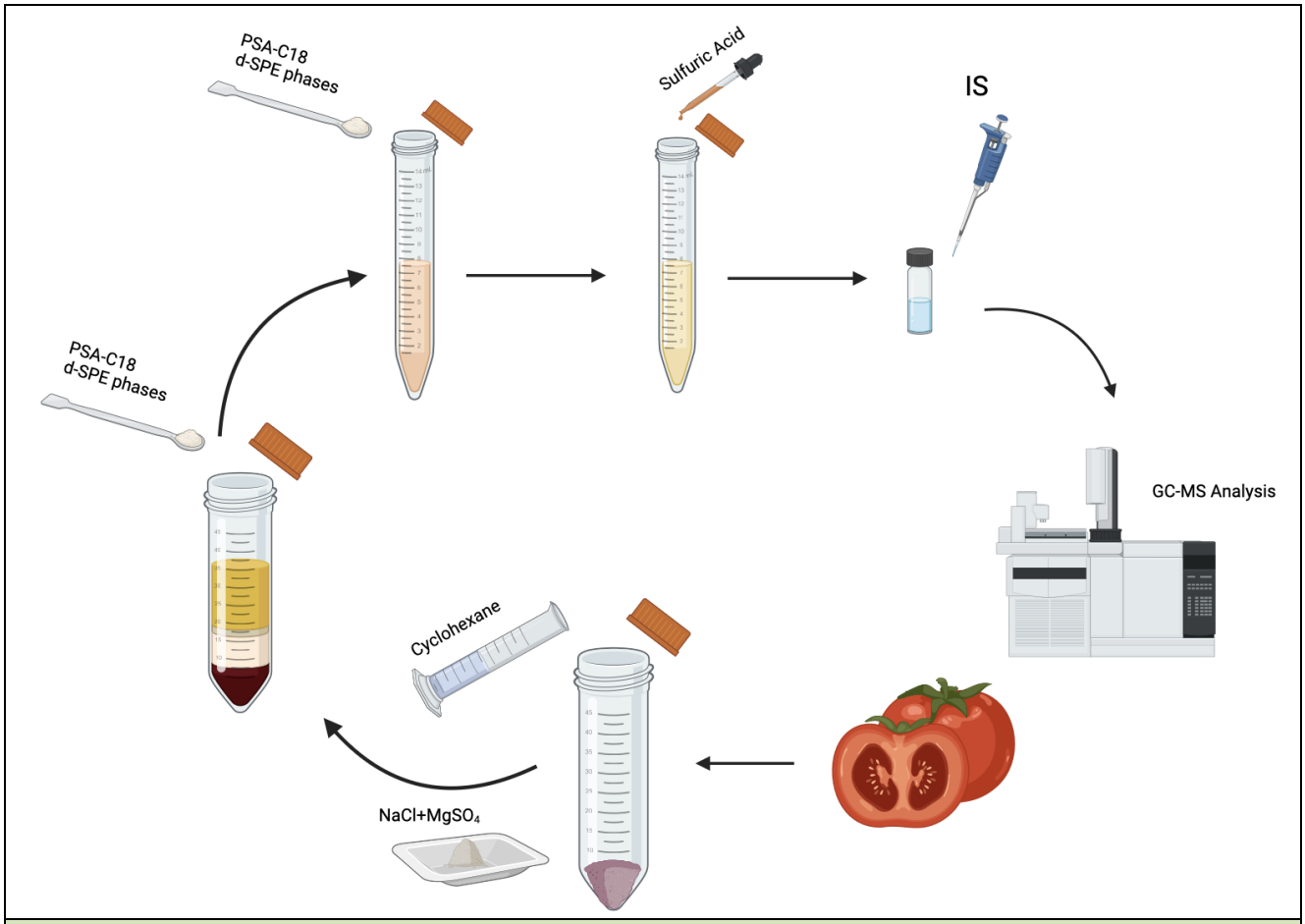

Figure 3 – QuEChERS procedure applied to tomato samples.

FOSC
ERA-NET Cofund on
Food Systems and Climate

This project has received funding from the European Union's Horizon 2020 research and Innovation programme under grant agreement No 862555

Firstly, we examined the extraction recoveries. Accuracy was checked through the addition of surrogate solutions into the samples, comparing the response of the extracted sample to the response of a solution containing the same surrogates in pure solvents.

In simpler terms, we verified how efficiently we could extract these contaminants from the samples. This approach ensures reliable results and the overall quality of our findings.

The validation results are shown in Figure 4, from which if is possible to see that there is no analyte with recovery percentage below 48% or above 110%. Also, recovery is not affected by matrix composition.

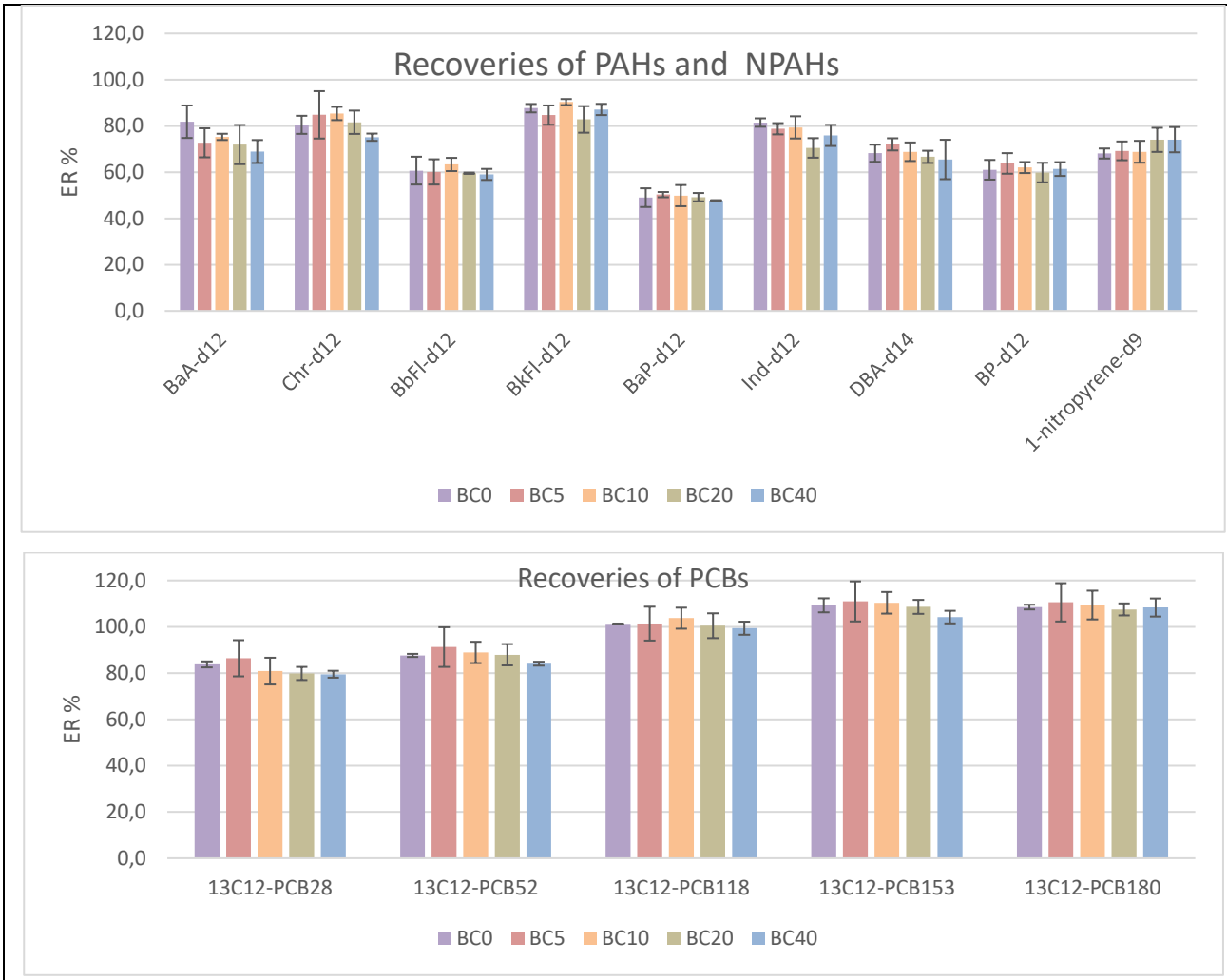

Figure 4 – Extraction recoveries of PAHs, NPAHs and PCBs.

This project has received funding from the European Union's Horizon 2020 research and Innovation programme under grant agreement No 862555

Once determined the extraction recoveries of PAHs, NPAHs and PCBs for each sample, the procedure has been used for the quantification of the target compounds in BC0, BC5, BC10; BC20 and BC40 tomato samples.

As shown in Figure 5 below, just Acenaphtene (AcPh) and Anthracene (Ant) were quantified in the samples. The concentration of contaminants in tomatoes are shown in table below.

Ant was also observed in tomatoes grown without biochar (BC0), and apparently increases with the biochar amount used for their growth. Since Ant was detected also in BC0, its presence seems to be related to a background contamination, either in the peat or in the environment (air). Nevertheless, the increase of Ant concentration from BC5 to BC40 could be ascribed to the presence of this compound in the biochar used.

AcPh contamination of the samples does not have an increasing pattern.

	BC0 Concentration (µg/kg)	BC5 Concentration (µg/kg)	BC10 Concentration (µg/kg)	BC20 Concentration (µg/kg)	BC40 Concentration (µg/kg)
AcPh	<MQL	<MQL	7,1±1.3	3,3±0.9	<MQL
Ant	4.3±0.5	6,7±1.4	11,8±2.2	12,6±3.2	11,6±2.2

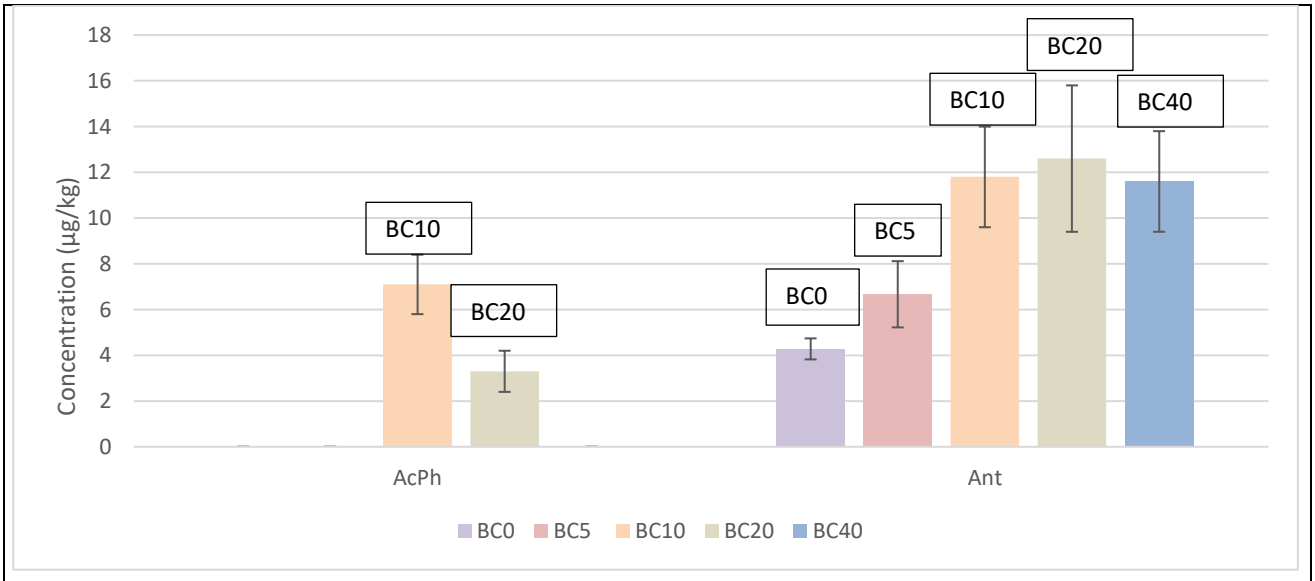

Figure 5 – Concentration of PAHs obtained for tomato grown with different percentage of biochar.

FOSC
ERA-NET Cofund on Food Systems and Climate

This project has received funding from the European Union's Horizon 2020 research and Innovation programme under grant agreement No 862555

In 2006, the European Union set maximum concentrations for specific PAHs in certain foods using BaP and the sum of BaA, BbFl, and Chr as markers (Regulation (EC) No 1881/2006). However, this regulation didn't include guidelines for vegetables. In 2020, Regulation (EU) 2020/1255 amended the 2006 regulation regarding PAH levels in certain foodstuff, but not for vegetables and fruits. Currently, there are no established concentration limits for vegetables and fruits. Interestingly, none of the samples in our study showed detectable levels of BaP, BaA, BbFl and Chr.

The concentrations of AcPh and Ant detected in our samples were compared to those found in studies conducted by *Araromi et al*. and *Huidong Li et al.* both on commercial tomato samples respectively from Nigeria and China. In the first study, similar concentrations of AcPh were reported, while Ant concentrations were lower compared to our findings. However, other PAHs not found in our samples were detected in their study.

Similarly, in the study by *Huidong Li et al.,* the concentrations of AcPh and Ant fell within the range determined in our study.

This work suggests that while biochar may contribute to Ant contamination in tomatoes, overall tomato contamination levels are comparable to those found in other commercial samples. This contamination is largely attributed to environmental factors, meteorological conditions, and transportation and storage conditions.

The contamination data will be used for human health risks assessment study. Moreover, it will be interesting to analyze the characterization data of the biochar used for the growth of tomato samples, to assess the possible source of these pollutants and to clarify, consequently, if the use of biochar in agriculture is safe for human health.

Araromi, A. A.; Ayodele, O.; Azeez, M. A.; Olanipekun, E. O. Assessment of Trace Organics in Tomatoes from Selected Markets in Ado-Ekiti, Nigeria. **2020**, 11.

Li, H.; Zhu, D.; Lu, X.; Du, H.; Guan, S.; Chen, Z. Determination and Risk Assessment of Sixteen Polycyclic Aromatic Hydrocarbons in Vegetables. *J. Environ. Sci. Health Part A* **2018**, *53* (2), 116–123. https://doi.org/10.1080/10934529.2017.1377573.

This project has received funding from the European Union's Horizon 2020 research and Innovation programme under grant agreement No 862555