EVALUATION OF ORGANIC AND INORGANIC MICRO-POLLUTANTS DURING THE COMBUSTION OF RICE STRAW

Guerriero E[1], Cerasa M[1], Mosca S[1], Colapicchioni V[1],Perilli M[1], Khalid A[2], Mahmood T[2], Gallucci F[3], Carnevale M[3], Paris E[3], Del Giudice A[3], Rotatori M[1]

[1] Institute of Atmospheric Pollution Research – IIA-CNR National Research Council of Italy – Monterotondo Scalo– Roma) Italy -00015 guerriero@iia.cnr.it

[2]Department of Environmental Sciences, Pir Mehr Ali Shah Arid Agriculture University, Shamsabad, Muree Road Rawalpindi – Pakistan

[3]LAS-ER-B Laboratory in Council for agricultural research and economics - CREA-IT Engineering and Agri-foodstuffs processing, Monterotondo, Roma Italy 00015

Introduction

Rice is an important cash crop, and it is estimated that 739 million tonnes were produced in 2016, leaving a significant amount of residue burned after harvest in the field, such as roots, stubbles and straw [1]. Over recent decades, it is an emerging and important issue contributing to the intensification of smog, especially in Asian countries. Open burning is a common practice in rice straw management in Asia[2]. Mass ratio between the obtained biomass waste and the rice produced is equal to 1.76 while the total waste burned in the world is about 20% [3]. Considering these data, it is clear that the annual burnt biomass of the world is equal to 260 million tonnes. This study aims to determine the amounts of atmospheric organic and inorganic micropollutants emitted during the burning of rice straw biomass, compared to wheat straw (PCDD/Fs, dl-PCBs, PAHs, metals, PM).

Materials and methods

The experimental campaign was carried out on basmati rice straw (*Oryza sativa*) especially imported from Pakistan from three different areas including Punjab, Azad Jammu and Kashmir (AJK) and Sindh, and wheat straw of the variety *Triticum Aestuvum L.* produced by CREA (Council for Agricultural Research and Economics). The biomass has been shredded and open-air dried in order to reduce the size and the moisture, thus facilitating the combustion process.

Boiler GSA/80 (D'Alessandro Termomeccanica Serie GSA 80KW) was used for combustion; the fuel was extracted from the circular modified hopper (for straws combustion) by means of special motorized blades that convey it towards the fall hole in the upper auger.
Biomasses were chopped to 4 mm before being sent in boiler as feed. The same biomasses were milled with a ball mill, homogenized and subsequently characterized to determine its chemical and physical characteristics (Table 2).

The boiler's stack was provided with several flanges to accommodate different kind of probes for flue gas sampling. The plant was stabilized for about 30 minutes as a test run for emissions.
For Particulate Matter, Metals, PCDD/Fs, PCBs and PAHs, the sampling system was equipped with a probe heated at 120±5 °C, a cooling device (6±2°C), a 47mm quartz fiber filter, and a pumping system able to ensure isokinetic conditions, necessary to avoid error caused by sampling the particulate matter, as requested by the European method UNI EN 13284-1[4] and EPA 201A [5].
According to UNI EN 13284[4], each sampling lasted an average of 30 min and was performed with an automatic isokinetic sampler (ST5, Dadolab) equipped with a Pitot tube and a thermocouple. A heated titanium probe with a heated out-stack (47mm) filter holder (Dadolab), both equipped with quartz microfiber filters without binders, have been utilized.
PCDD/Fs and dl-PCBs and PAHs were isokinetically sampled according to methods EN-1948-1 and 4[6-9] and ISO 11338-1[11], respectively. The metals were isokinetically sampled with the same system, replacing the adsorbent part (condenser and XAD-2) for the semi-volatile organic compounds with 3 bubblers containing HNO_3/H_2O_2 as absorbing solutions. The metal content was determined by means of the ICP-MS 7700 (Agilent) according to the UNI EN ISO 17294-2[12] after samples mineralization. Metals were determined by using the EN 14385 method[13].
The determination of PCDD/Fs and PCBs was performed according to EN 1948-2,3,4 methods [7-9] while for the PAHs the method ISO 11338-2[14] was used . The gas chromatography/mass spectrometry (GC/MS) analyses were run on a TSQ 8000 Evo (Thermo Scientific)[15-16].

Results and discussion

In table 1 the gas stack emission concentrations are reported. The comparison between rice straw and wheat straw do not show significant difference in terms of PCBs content, while different quantity of PCDD/Fs were recorded. It is interesting to observe that the total concentration of both PCDD/Fs and PCBs, expressed as TEQ pg/Nm^3, resulted from the rice straw combustion, is one order of magnitude higher than the quantity obtained from the wheat straw combustion. These data can be justified on the basis of the catalytic effect of the copper in of organo-chlorine compounds formation during combustions[17-18]. On the other hand, the values obtained from the combustion performed by using the boiler are one order of magnitude lower than the combustion realized in open burning and these findings are in good agreement with the literature. [1]

Table 1 –Comparison of the biomass combustion in terms of concentrations of flue gas stack emission of micro organic pollutants, particulate matter (PM) and Cu

	Σ PCDD/Fs	Σ dl-PCBs	Σ PCDD/Fs and dl-PCBs	Σ PAHs	Total PM	Cu
	TEQ(pg/Nm^3)	TEQ (pg/Nm^3)	TEQ(pg/Nm^3)	(μg/Nm^3)	(mg/Nm^3)	(μg/Nm^3)
Wheat Straw Triticum Aestuvum L.	2,9	15,8	18,7	362	31	10,6
Rice 1 Punjab	210,7	12,0	222,7	460	26	35,0
Rice 2 AJK	759,8	52,8	812,6	488	61	47,5
Rice 3 Sindh	94,3	18,2	112,5	483	89	21,7

The ash content in rice straw – as shown in Table 2 – results to be the double of the wheat straw ash, and this results in a higher cupper content in emissions (refer to table 1). The high concentration of ashes influences also the combustion, in fact, even operating in an excess of oxygen, high concentrations of carbon monoxide were recorded. It suggests that the combustion of straw is a "bad combustion", since the high content of ash does not allow that the combustion is performed in a homogeneous phase between the comburent and the fuel.

Table 2- Characterization of biomass before being burned in the boiler

	Characterization of Biomasses				Elementary Analysis				
	Moisture on a dry basis %	Ashes average %	Highest Calorifying Power MJ/Kg	Lower Calorific Value MJ/Kg	C %	H %	N %	S %	O %
Wheat Straw Triticum Aestuvum L.	10,59	7,6	17,0	15,7	43,2	6,1	0,6	1,7	40,8
Rice 1 Punjab	9,33	18,2	14,7	13,5	36,4	6,0	0,8	0,1	38,6
Rice 2 AJK	9,64	17,1	14,5	13,4	38,3	5,6	0,7	0,1	38,4
Rice 3 Sindh	10,15	15,6	14,9	13,7	37,3	6,0	0,5	0,1	40,5

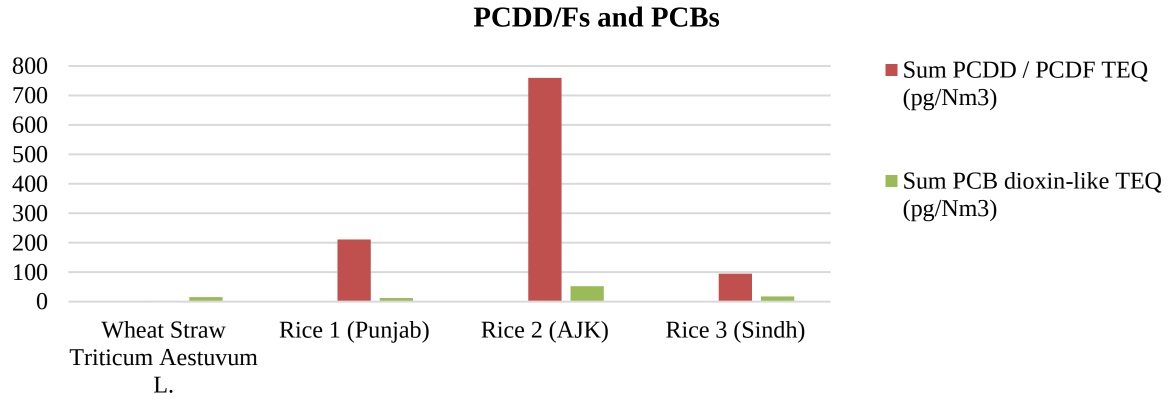

Figure 1 – Total concentration of PCDD/Fs and PCBs expressed as TEQ pg/Nm^3

In this investigation were analyzed PAHs refers to 4- to 6-ring compounds, moreover, the PAHs concentrations are higher than that obtained from the wood biomass combustion[19].
This experimental campaign highlights how both wheat and rice straw combustions emit relevant concentrations of organic and inorganic micropollutants. In particular, the high concentrations of PCDD/Fs and PCBs emitted during the rice straw combustion, could be related to the presence of copper which can used as fungicide during seeding.

References:

1. Oanh N.T. K, BichaT. L., TipayaromaD. T., ManadharaB. R., PrapataP., SimpsonbC. D., and LiuL-J S., (2011) *Atmos. Environ*. 1; 45(2): 493–502.
2. Gaddea B., Bonneta S., Menkeb C. GarivaitaS., (2009) *Env. Pollution*, 157 (5) :1554-1558
3. Streets, D. G., K. F. Yarber, J.-H. Woo, and G. R. Carmichael (2003) *Global Biogeochem. Cycles*, 17(4), 1099.
4. UNI EN 13284-1, (2017) *Milan, Italy: (Eds) UNI*
5. EPA Method 201a (2018)
6. UNI EN 1948-1, (2006) *Milan, Italy: (Eds) UNI*
7. UNI EN 1948-2, (2006). *Milan, Italy: (Eds) UNI*
8. UNI EN 1948-3, (2006) *Milan, Italy: (Eds) UNI*
9. UNI EN 1948-4, (2014) *Milan, Italy: (Eds) UNI*
10. UNI EN ISO 17294-2, (2016) Milan, Italy: (Eds) UNI
11. ISO 11338-1, (2003)
12. UNI EN ISO 17294-2 (2016) Milan, Italy: (Eds) UNI
13. UNI EN 14385, (2004) *Milan, Italy: (Eds) UNI*
14. ISO 11338-2, (2003)
15. P Benedetti, E Guerriero, S Mosca, M Rotatori (2017) *Journal of Separation Science* 40 (17): 3469-3478
16. Guerriero, E., Guarnieri, A., Mosca, S., Rossetti, G., Rotatori, M., (2009) *Journal of Hazardous Materials*. 172: 1498-1504.
17. Huang H, Buekens A., (1995*) Chemosphere*: 31:4099 –4117.
18. Vogg H, Kreisz S, Hunsinger H. (1994) *Organohalogen Compd*, 20, 305 –307
19. B. M. Jenkins, A. D. Jones, S. Q. Turn, R. B. Williams (1996) *Env. Sci. & Techn.30* (8): 2462-2469