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Article

Estimation Inventories of POPs from Rice Straw Combustion as an Agricultural Waste

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Abstract: Rice cultivation is the main agricultural activity in Asia, and it results in an enormous amount of agricultural waste, that are usually disposed-off by burning, causing serious environmental health and climate problems. Pakistan is the tenth largest producer in the world and the fourth exporter of rice in the world. To date, there are no studies targeting Pakistan's profile monitoring its contribution in open burning emissions from rice straw waste. This study presents the characterization of PCDD/Fs, PCBs and PAHs emissions from three samples of rice straw collected from the main rice cultivation regions of Pakistan (Punjab, Sindh and Azad Jammu and Kashmir) in relation to the role of metal-based agricultural additives. PCDD/Fs, PCBs and PAHs emissions were quantified using a fixed grid system biomass plant and measuring the macro-pollutants online and sampling the organic micro-pollutants and metals in isokinetic mode, followed by ISO and CEN standards methods. In addition, role of agrochemicals was monitored in terms of metal catalysis resulted in POPs emissions. This study provides the characterization of most relevant group of pollutants (metals, PCDD/Fs, PCBs and PAHs) as a result of agricultural waste combustion. The rice straw samples from AJK showed high values of organochlorine micro-pollutants compared to the values followed by samples from Punjab and Sindh, i.e., respectively, ∑PCDD/F (2594>1493>856 pg/Nm^3) and ∑PCB (41>38>30 pg/Nm^3). Whereas the organic micro-pollutants ∑PAH, indicators of incomplete combustion (PICs), were recorded high in the samples from Sindh followed by Punjab and AJK. This study supports the idea that the phenomena that lead to the formation of PCDD/F and PCB are influenced not only by poor combustion but also by the presence of metal catalysts or precursors in the burned fuel.

Keywords: agricultural waste; atmospheric pollution; dioxins; emission inventory; metals; POPs; risk assessment; rice straw

1. Introduction

The agricultural system of paddy fields is linked to the production of massive quantities of crop waste after each harvest, which includes roots, stubble and straw [1]. The world annual rice crop production is 700 million tons, which globally produced 80 % of crop residue (2.8 billion tons) for 158 million tons of rice harvested only in Asia [2] (632 million tons of crop residue), as it is calculated that the grain-to-straw ratio varies between 0.5 and 0.7 for rice crop [3]. The common disposal of rice straw is through open field burnings and in Asian countries, where this crop represents the economic pillar, this practice represents an important source of pollution [4]. Pakistan contributes 1.7% to the total rice production of Asia, ranking as the tenth producer and fourth exporter [5]. Rice is usually planted in Pakistan during the summer season, around May/June, and harvested around October/November, followed immediately by the cultivation of wheat. The short time between rice harvesting and wheat cultivation leads farmers to dispose-off agricultural residues through open

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burnings [6]. Currently, POPs emissions from biomass combustion represents a huge environmental and health problem for the population of Pakistan. The main territories of Pakistan where rice is grown include the provinces of Sindh and Punjab, and the neighbouring regions of State of Azad Jammu and Kashmir (AJK) [7].

In addition to the internal sources, we must also add the contribution due to the main neighbouring rice producers (such as China and India) through the transboundary movement of aerosol [8, 9] because both local combustion and transboundary movement of aerosols contributes in local regional air pollution. Prior to this study, the environmental conditions in Pakistan have not been subject to systematic monitoring and evaluation. Therefore, the data obtained from this investigation provides novel insights into the current situation regarding emissions of PCDD/Fs, PCBs and PAHs. Furthermore, the examination of metal emissions aimed to assess the potential impact of agricultural additives on the catalytic activity of chlorinated compounds. Consequently, these findings represent a significant step forward in understanding and addressing the environmental challenges faced in Pakistan.

From 2015 to 2022, the production of rice in Pakistan increased by 4.6 %, equal to 7.5 Mt of rice produced, and with it the combustion of its residues (consequently the emission of pollutants) [5]. During the combustion of rice straw Brown Clouds are formed, consisting of Particulate matter (PM), nitrogen oxides and Black Carbon (BC) [10]. Due to the poor combustion conditions in the absence of oxygen (oxidizer) caused by the piles, the combustion of rice straw generally produces a large amount of BC. This phenomenon is amplified by the high amount of silica present in this type of straw, which produces sintered forms of ash/fuel/silica that prevent the homogeneous phase oxidation reactions and reduce the oxygen/fuel contact [11]. Given the high adsorbing power of PM and BC, they could represent a vehicle for persistent organic pollutants (POPs) that can be generated by bad combustion including , polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) [11–16].

The formation of halogenated POPs comes from the catalytic action for some metals such as the oxides of Cu and Fe [17, 18]. These metals are constituent parts of the additives (pesticides, fungicides, herbicides and fertilizers) used on agricultural crops [19; Supplementary material Table S1] and they have been detected in biomass combustion emissions [20–22]. It must be taken into account that the agricultural additives absorbed by the rice plants and accumulated in the straw cannot be linked only to this crop. Part of these additives are absorbed by the soil and therefore also derive from the cultivation of wheat for which the same land area was used [© 2021 Syngenta PAKISTAN - Wheat, 2021 Supplementary material Table S2; 23].

Studies conducted by Palma et al. [24] and Carnevale et al. [25] showed that prominent metals emitted by combustion of agricultural residue waste includes Fe, Cu, Zn, Na, Mg, K and Ca. Experimentation led by Mubeen et al. [26] concluded that when metals combined by Cl exposed to combustion conditions resulted in dioxin emissions among which $CuCl_2$ is the major contributor in TEQ values. Dioxin emissions are intensifying compared to previous cultures precisely due to the application of pesticides, for example in Hokkaido (Japan) atmospheric values rise from 0.0058 to the existing 0.53 pg-TEQ/m^3 [27]. Human exposure to atmospheric chemistry culprits is currently a major problem and rising with every passing year. Respiratory illnesses increased to three folds in biomass combustion zones [28]. Yao et al. [29] and Zhang et al. [30] reviewed studies on PAH emissions as a result of biomass combustion and concluded that moisture content, cellulose and lignin characterization of straw type and emerged volatile compounds accelerated PAH emissions.

The data here reported are part of a larger project in collaboration between the Department of Environmental Sciences of the Pir Mehr Ali Shah Arid Agriculture University Rawalpindi, the Italian National Research Council's Institute of Atmospheric Pollution Research (CNR-IIA), and the Council for Agricultural Research and Economics Center of Engineering and Agro-Food Processing (CREA-IT). Agricultural waste from the three main regions involved in rice cultivation in Pakistan (Punjab, Sindh and Azad Jammu and Kashmir (AJK)) were compared by burning through a boiler. The project included the characteristics of rice straw residues in combustion and the emissions characterization considering the elemental analysis, the metals content and the quantification of PCDD/Fs, PCBs and

PAHs for each type of straw. Furthermore, the influence that the metal content has on the formation of the organochlorines detected was evaluated.

2. Materials and Methods

2.1. Rice straw samples

The experimentation was carried out on rice straw (Oryza sativa L.), imported from three different localities in Pakistan: Shakargarh, Punjab, Mirpur, Azad Jammu and Kashmir (AJK) and Sukkur, Sindh. Composite samples weighing 200 kg each, were collected from randomly selected localities of each selected area. Firstly, the samples were brought to Chakwal Koont agricultural farm of Pir Mehr Ali Shah Arid Agriculture University Rawalpindi for the period of one week. Later the samples were transported to Milan port of Italy from Karachi port of Pakistan via ship cargo where all facilities were provided for secure storage of sample. In Italy after reaching at CNR-IIA storage facility characteristics test for rice straw has been performed as described in Table 1.

2.2. Boiler and Sampling

A fixed grid system biomass boiler in the combustion phase GSA 40-80 kW (D'Alessandro Termomeccanica, Italy) was used as the combustion plant. Under the grid on which the rice straw sample was stored, a fan distributed the air. A double auger mechanism was operated that transported the biomass to the combustion chamber from storage chamber powered by mechanical system. Sampling for PCDD/Fs, PCBs and PAHs were performed according to an internal method based on EN 1948 reference methods (UNI EN 1948-1:2006, 2006; UNI EN 1948-4:2014, 2014). Sampling was conducted using an ST5 Isokinetic auto-sampler pump (DadoLab, Italy) connected to a titanium probe (Isokinetic Heated Probe HP5 DadoLab, Italy), which was separately used to collect both organic micro-pollutants and metals.

Briefly, PCDD/Fs, PCBs and PAHs analysis were collected through a quartz thimble containing quartz wool (Munktell, Ahlstrom-Munksjö, Finland) heated up to 120 ± 5 °C. The condensed vapours (6 ± 2 ° C) and the gaseous fraction of samples were adsorbed on XAD-2 (Amberlite, Merck, Germany). At the end of each sampling, the probe was washed with 200 mL Methanol, Acetone and Dichloromethane. Prior to the sampling, a Sampling Standard solution containing isotopically labelled (^{13}C) congeners of PCDD/Fs and PCBs was added to the quartz wool present in the sampling thimble.

As for the analysis of the metals, a quartz fiber filter (QFF) (MK-360 Munktell) was used and 3 bubblers were inserted downstream containing a solution of HNO_3/H_2O_2 (3.3% $_{w/w}$/1.5%$_{w/w}$), according to [31] for the collection of the volatile fraction. After sampling, the entire probe was washed with the 200ml HNO_3 25%$_{w/w}$ solution. The samplings were carried out between 22/11/2017 and 06/12/2017 (Supplementary material Table S4). Each sampling involved laboratory blanks and field blanks that underwent the same treatment as the samples. To ensure control and quality assurance of the entire procedure, blanks were subtracted from real samples.

2.3. Standards and Solvents

All ^{13}C and per deuterated standard solutions of PCDD/Fs, PCBs and PAHs were purchased from Wellington Laboratories, Canada. The Sampling Standard solution contained 13C-PCBs (P48-SS, 10 pg/µl) and 13C-PCDD/Fs (EN-1948SS, 10-20 pg/µl). The Extraction Standard solution contained ^{13}C labelled PCBs and PCDD/Fs (WP-LCS, 10pg/µl and EN-1948ES, 10-20 pg/µl, respectively). As for PAHs, the Extraction standard solution contained per deuterated compounds (L-429IS, (10 ng/µl). Finally, EN1948-IS (10-20 pg/µl), WP-ISS (10 pg/µl) and L-429RS (10 ng/µl) were used as Injection Standards solutions for PCDD/Fs, PCBs and PAHs, respectively. The GC/MS calibration was performed by the isotopic dilution method, using commercially available calibration curves: EN1948-CVS for PCDD/Fs, P48-W-CVS for PCBs and PAH-CVS-B for PAHs (Wellington Labs). The mix Standard solution used for ICP-MS calibration was taken from Merck. Acetone (Ace), methanol (MeOH), toluene (Tol), dichloromethane (DCM), n-Hexane (Hex) used in the chemical analysis were purchased from Romil (UK), the MilliQ water from Millipore, Merck, Germany while the HNO3 by Merck (Germany).

2.4. Cleanup and Analysis

2.4.1. PCDD/Fs, PCBs and PAHs

The samples collected were taken to the laboratory for processing. Each sample for micro-pollutants analysis consisted of a Thimble, XAD-2 cartridge, the probe condensation water and the probe washes solution. The condensed water was extracted by Liquid/Liquid (L/L) extraction with DCM (10% of the total volume) by adding an amount of NaCl (25g) to increase the ionic strength. The extraction was performed 3 times collecting all the extracts in the same flask. The XAD-2 was placed in the Thimble with 4 g of Na_2SO_4 and the probe wash solution. The whole thimble was extracted in Soxhlet for 36h with toluene after adding the Extraction Standards Solutions of PCDD/Fs and PCBs (500 pg).

The Soxhlet and the L/L extracts were combined in the same round bottom flask to be concentrated in rotary evaporator up to a volume of 10 ml. The extract was divided into two aliquots: PAHs analysis was carried out on, 1/10 of the concentrated extract, and the remaining 9/10 of the extract was used for PCDD/Fs and PCBs clean-up and separation, performed by following Guerriero et al. [32]. The two fractions containing PCDD/Fs and PCBs were concentrated and spiked with ^{13}C labelled Injection Standards Solutions (WP-ISS and EPA1613-IS for PCBs and PCDD/Fs, respectively). PCDD/Fs and PCBs were analysed by a triple quadrupole GC/MS (Trace 1310 GC/TSQ 8000 Evo, ThermoScientific, US); the chromatographic separation was carried out on a DB-XLB column (60 m, 0.25 mm, 0.25 mm ID, Agilent J&W) using hydrogen as the carrier gas [33].

The 1/10 of the extract dedicated to the analysis of PAHs, was spiked with the Extraction Standard (L429-IS) and then cleaned-up on a manually packed micro-column (1 g of 3% deactivated basic alumina and 3 g of activated silica) eluted with DCM:Hex 50:50. The eluate was concentrated and then added with labelled Injection Standard Solution. PAHs analysis was performed on a DSQ II Single Quadrupole GC/MS (Trace GC Ultra/DSQ II, Thermo, US). The separation was performed on Rxi@-5ms column (30 m length x 0.25 µm film thickness x 0.25 mm ID, Restek, USA).

2.4.2. Metals

The metals analysis was performed in accordance with ISO 17294-2(2016) using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS 7700 Agilent). The QFF was transferred into a Teflon Vessel and subjected to acid attack by a microwave digester (Start D, Milestone, Italy). The acid attack was carried out with a solution of 6 ml of HNO3 (65%) and 3 ml of H_2O_2 (30%). The probe washes were filtered with a second QFF, which was extracted as above. The extract and the filtrate were unified and added to the more volatile part collected by the solution of the two bubblers. The sample was brought to a final volume of 100 ml after the addition of ultrapure water and subjected to analysis. The calibration of the instrument was performed using multi-element standards (Standard mix, 10 ppm metal concentration, Christiansburg, Virginia, USA), prepared in aqueous solution acidified with 1% of HNO_3 Instrumental calibration was performed with 5 standards of increasing concentrations (from 5 to 100 ppb). The Yttrium (Merck, Germany) was used as an internal standard through the automatic input system provided by the instrument.

2.5. Emission factors

Consider the calculation of the emissivity factor as follows (Equation1)

$EF=(X \cdot \text{flow rate dry})/B$ Equation 1

EF: Emission factor expressed in TCDD TEQ pg/kg for PCDD/Fs and PCBs and in B(a)P TEQ µg/Kg for c-PAHs

X: Summation of the concentrations of each congener of the class expressed in TCDD TEQ (pg/Nm3) for PCDD/Fs and PCBs and in B(a)P TEQ (µg/Nm3) for c-PAHs.

flow ratedry: average dry flow rate in Nm3/h.

B: Kg/h of biomass burned

3. Results

3.1. Biomass characterization

Biomass characterization was observed as mentioned in Table 1. The characterization was carried out before sample combustion. The high content of average ash % represents the high silica content as result of combustion. It also enhances the bad combustion conditions in boiler bed that inhibits the pollutants emissions [25], that is discussed in coming sections in detail.

Table 1. Characterization of rice straw biomass (Mean values and standard deviations obtained by performing three measurements on three distinct samples of the biomass).

Characteristics	Punjab	AJK	Sindh
Moisture on a dry basis %	9.3 ± 0.3	9.6 ± 0.3	10.2 ± 0.4
Ashes average %	18.2 ± 0.2	17.1 ± 0.2	15.6 ± 0.2
Highest Calorific Power (MJ/Kg)	14.7 ± 0.4	14.5 ± 0.4	14.9 ± 0.4
Lower Calorific Value (MJ/Kg)	13.5 ± 0.4	13.4 ± 0.4	13.7 ± 0.4
C %	36.4 ± 0.2	38.3 ± 0.2	37.3 ± 0.2
H %	6.0 ± 0.1	5.6 ± 0.1	6.0 ± 0.1
N %	0.8 ± 0.2	0.7 ± 0.2	0.5 ± 0.2
S %	0.1 ± 0.2	0.1 ± 0.2	0.1 ± 0.2
O %	38.6 ± 0.4	38.4 ± 0.4	40.5 ± 0.4

3.2. Metals

As a reference, the current legislation for plant emissions was taken into consideration, i.e. the European Directive (EU) 2015/2193 which identifies the limits for the total content of metals in the fumes (European Commission, 2015). The concentrations of metals recorded in the emissions of the three samples of straw are justified by the type of combustion system (Table 2). The study of metals was aimed at evaluating whether the presence of specific species during combustion acted as a catalyst for the formation of organic chlorinated micro-pollutants. Among these metals it is known that copper (Cu) is the one that favours the formation of organochlorine micro-pollutants while other metals such as Zinc and Cadmium have significantly lower catalytic activity [34]. From Table 2, it can be observed that the Cu in the AJK rice straw sample reaches 47.5 μg/Nm^3, greater than the sample from Punjab 35.0 μg/Nm^3 and more than double compared to the rice straw samples from Sindh (21.7 μg/Nm^3). Palma et al. [14] supports the same trends in relation to metal's catalytic action in the formation of PCDD/Fs and PCBs. The other metals, on the other hand, have very different trends. For example, Fe is lower in AJK rice straw (78 μg/Nm^3) but act as a powerful precursor due to effective catalytic activity along with Cu (22-48 μg/Nm^3) in formation of PCBs and PCDD/Fs. Mg, Ca, Fe and Zn showing the top emerging metals might be the result of irrigation water and fertilizers used for crop growth [14, 35].

Table 2. Metal concentrations (μg/Nm^3) in the emissions of the three straw samples from the regions of Punjab, AJK and Sindh (Mean values and standard deviations obtained by conducting three measurements on the same emission sample).

Metals	**Punjab (μg/Nm^3)**	**AJK (μg/Nm^3)**	**Sindh (μg/Nm^3)**
Mg	321 ± 7	611 ± 10	691 ± 10
Al	82 ± 2	53 ± 2	98 ± 2
Ca	362 ± 7	486 ± 9	370 ± 7
Cr	4.9 ± 0.1	2.2 ± 0.1	4.3 ± 0.1
Mn	18.3 ± 0.4	30.4 ± 0.6	32.9 ± 0.7
Fe	113 ± 2	78 ± 2	106 ± 2
Co	1.3 ± 0.1	0.1 ± 0.1	0.2 ± 0.1
Ni	11.1 ± 0.3	9.9 ± 0.3	6.2 ± 0.2
Cu	35 ± 1	48 ± 1	22 ± 1
Zn	134 ± 3	89 ± 2	93 ± 2
Sr	4.9 ± 0.2	22.2 ± 0.5	16.6 ± 0.4
Ag	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.1
Cd	0.9 ± 0.1	0.8 ± 0.1	0.4 ± 0.1
Ba	1.9 ± 0.1	4.4 ± 0.1	3.8 ± 0.1
Tl	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1
Pb	13.5 ± 0.3	14.5 ± 0.3	14.4 ± 0.3
Bi	4 ± 0.1	7.2 ± 0.1	8.8 ± 0.2

3.3. PCDD/Fs, PCBs and PAHs

Rice straw has a high content of Silica (10 - 15%) which tends to polymerize in the cell wall of the epidermis at high temperatures [36], rice straw also contains cellulose (32% to 47%), hemicellulose (19% to 27%) and lignin (5% to 24%), the latter known as lingo-cellulosic biomass [34, 35]. Compared to other biomasses, rice straw is considered a low-performance fuel due to its low calorific value [39]. It is apparent from Table 3 that high quantities of micro pollutants were produced by the combustion tests of three rice straws samples. The distribution of PCDD/F, PCB and PAH classes varies significantly depending on the types of rice straw, i.e., a characteristic fingerprint for rice straws is not obtained, even when using similar combustion conditions and as observed from Table 1, the macro-constituents of the fuels appear to be similar. The PCDD/Fs concentrations in the emissions from AJK rice straw are significantly higher than the others (2594 TEQ pg/Nm^3). The Deacon reaction for dioxin formation explains the higher production in AJK as higher Cu concentrations enhance the emissions.

Table 3. PCDD/Fs concentrations and it's TEQs for rice straw samples in reference to International toxicity equivalency factors (I-TEFs NATO 1988).

		Punjab		**AJK**		**Sindh**	
Compound	I-TEF	pg/Nm^3	TEQ (pg/Nm^3)	pg/Nm^3	TEQ (pg/Nm^3)	pg/Nm^3	TEQ (pg/Nm^3)
2,3,7,8-TetraCDD	1.000	7.3	7.34	86	86.07	8.0	7.97

1,2,3,7,8-PentaCDD	0.500	127	63.48	931	465.35	19	9.43
1,2,3,4,7,8-HexaCDD	0.100	3.2	0.32	51	5.11	4.9	0.49
1,2,3,6,7,8-HexaCDD	0.100	6.4	0.64	652	65.16	1.6	0.16
1,2,3,7,8,9 Hexa-CDD	0.100	3.2	0.32	21.9	2.19	1.6	0.16
1,2,3,4,6,7,8-HeptaCDD	0.010	223	2.23	1240	12.40	504	5.04
OctaCDD	0.001	28722	28.71	127646	127.64	26675	26.66
2,3,7,8-Tetra CDF	0.100	9647	964.27	8512	851.20	6472	646.89
1,2,3,7,8-PentaCDF	0.050	4321	215.95	12833	641.62	2485	124.21
2,3,4,7,8-Penta CDF	0.500	225	112.28	450	225.14	39	19.51
1,2,3,4,7,8-HexaCDF	0.100	581	58.05	637	63.70	37	3.74
1,2,3,6,7,8-HexaCDF	0.100	102	10.21	15	1.46	31	3.09
2,3,4,6,7,8-HexaCDF	0.100	99	9.89	53	5.35	1.6	0.16
1,2,3,7,8,9-HexaCDF	0.100	12.8	1.28	2.4	0.24	4.9	0.49
1,2,3,4,6,7,8-HeptaCDF	0.010	1149	11.48	3525	35.25	797	7.97
1,2,3,4,7,8,9-HeptaCDF	0.010	64	0.64	438	4.38	16.3	0.16
OctaCDF	0.001	5744	5.74	1702	1.70	325.3	0.33
Sum PCDD/Fs		51037	1492.82	158795	2593.97	37424	856.44

In the three rice straw samples, there is a clear dominance of 2,3,7,8 TetraCDF and 1,2,3,7,8 PentaCDF compared to other congeners. Sum PCDD/Fs TEQ are higher in AJK rice straw sample followed by Punjab and Sindh. But the significantly higher emission of 2,3,7,8 TetraCDF observed from Punjab sample is 964 pg/Nm^3. It is following by the emissions of 1,2,3,7,8 PentaCDF recorded as 642 pg/Nm^3 (AJK) and 1,2,3,7,8 PentaCDF notified as 465 pg/Nm^3. All values were correlated with I-TEFs NATO 1988 recommendation index for TEF. Based on the results these three compounds potentially contributed to the total PCDD/Fs findings. Combustion conditions in support to addition of metals as catalysts (Cu or Fe) [25], or inhibited combustion conditions as in case of rice straw due to high silica and lignocellulose content [40]. Literature is also supporting the fact that thermal decomposition of lignocellulose material favours the formation of phenols that resulted in precursor route of dioxin formations [41].

Data from Table 4 is revealing an interesting phenomenon as PCDD/Fs data. The significantly higher sum PCB data revealed by AJK rice straw samples (41 dl-TEQ pg/Nm^3) followed by Punjab (38 dl-TEQ pg/Nm^3) and Sindh (30 dl-TEQ pg/Nm^3) likely to sum PCDD/Fs concentrations. Considering the PCBs values detected in three straw samples in relation to TEFs articulated by WHO 2006 guidelines (Table 4). Table is quite revealing in several ways as noticed highest TEQ was emitted by 3,3',4,4',5-PentaCB as 38 pg/ Nm^3 (AJK) followed by 35 pg/ Nm^3 (Punjab) and 26 pg/ Nm^3 (Sindh). Interestingly collective highest emissions were emerged from Sindh rice straw samples (87255 pg /Nm^3) but TEQs conflict the trend and AJK (41 dl-TEQ pg/Nm^3) shows rise as a result. That might be due to the highest results obtained for 3,3',4,4',5-PentaCB and its highest WHO-TEF.

Table 4. PCB amounts in pg and concentrations in Toxicity Equivalent (TEQ pg/Nm^3) of Punajb, AJK and Sindh rice straw samples.

		Punjab		AJK		Sindh	
Compounds	**WHO TEF 2006**	**pg/Nm^3**	**TEQ (pg/Nm^3)**	**pg/Nm^3**	**TEQ (pg/Nm^3)**	**pg/Nm^3**	**TEQ (pg/Nm^3)**
3,4,4',5-	0.0003	153	0.046	340	0.1021	263	0.0790

TetraCB							
3,3',4,4'-TetraCB	0.0001	4018	0.401	2966	0.2966	1773	0.1772
2',3,4,4',5-PentaCB	0.00003	405	0.012	2896	0.0868	867	0.0259
2,3',4,4',5-PentaCB	0.00003	29258	0.878	33910	1.0172	44926	1.3471
2,3,4,4',5-PentaCB	0.00003	683	0.021	652	0.0195	865	0.0259
2,3,3',4,4'-PentaCB	0.00003	10292	0.308	8721	0.2616	7393	0.2216
3,3',4,4',5-PentaCB	0.1000	351	35.088	1255	37.6853	263	26.337
2,3',4,4',5,5'-HexaCB	0.00003	16046	0.481	23623	0.7086	30071	0.9017
2,3,3',4,4',5-HexaCB	0.00003	466	0.013	2152	0.0645	529	0.0158
2,3,3',4,4',5'-HexaCB	0.00003	124	0.003	238	0.0071	169	0.0050
3,3',4,4',5,5'-HexaCB	0.03000	32	0.956	12	0.3646	13	0.3901
2,3,3',4,4',5,5'-HeptaCB	0.00003	163	0.004	102	0.0030	122	0.0036
∑ dl-PCB		**61991**		**76867**		**87255**	
∑PCB dioxin-likeTEQ			**38**		**41**		**30**

Chlorinated compounds originated from pesticides or fertilizers were supposed to be responsible for dioxin emissions as a result of combustion [14,24,42]. These compounds are normally not specifically related to combustion. In fact, they are found mostly in ambient air sampling and especially in urban areas [43]. We have higher dioxin emissions than reviewed literature in case of PCBs [14] and that was supposed to be due to bad combustion conditions during rice straw experiment [44]. Several scientific evidences show how this metal acts as a catalyst during combustion according to the synthesis of Deacon in the formation of chlorinated compounds [45,46]. Cu derives mainly from the fungicide treatments to which the rice crop is subjected during various stages of growth. As reported in the list of supplementary materials, more than one fungicide contains the metal Cu, i.e. copper oxychloride and cuprous oxide, or in a mixture of products such as Bordeaux and Moltovin (see Supplementary Material Table S1).

The concentrations of PAHs compared to those of PCDD/Fs and PCBs are significantly higher (Table 5). 14 PAHs were quantified during current study including carcinogenic compounds (benzo(a)anthracene, benzo(b+i)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, chrysene, dibenzo(a,h)anthracene, and indeno (1,2,3-cd) pyrene), as notified by USEPA (1998) and European Council (2004). Sum PAHs were considerably higher in Sindh (18536 ng/Nm^3) followed by Punjab rice straw sample (15353 ng/Nm^3) and

Table 5. Distribution in ng/Nm³ of PAHs congeners in the three types of rice straw: Punjab, AJK and Sindh.

Compounds	TEF	Punjab (ng/Nm³)	AJK (ng/Nm³)	Sindh (ng/Nm³)
Phenanthrene	0.0005	112	123	114
Anthracene	0.0005	9	33	14
Fluoranthene	0.05	3452	2687	3398
Pyrene	0.001	53	36	56
Benzo(a)anthracene	0.005	69	74	84
Chrysene	0.03	1262	962	1222
Benzo(b)fluoranthene	0.1	731	576	699
Benzo(k)fluoranthene	0.1	262	188	207
Benzo(e)pyrene	0.002	16	13	21
Benzo(a)pyrene	1	6779	7300	10327
Perylene	-	0	0	0
Indeno(1,2,3,c,d)pyrene	0.1	540	839	518
Dibenzo(a,h)anthracene	1.1	1980	2285	1787
Benzo(g,h,i)perylene	0.02	89	91	88
∑ PAHs		**15353**	**15207**	**18536**

AJK (15207 ng/Nm³). Benzo(a)pyrene had highest TEF value [47] that is also the contributing factor for highest values from straw samples ranged between 6779 to 10327 ng/Nm³ dominated by Sindh having greater toxicity threats. Sindh samples were also observed the rising trend of Fluranthene by 3398 ng/Nm³ followed by Dibenzo(a,h)anthracene (1787-2285 ng/Nm³). Moisture percentage, metal catalysts and high lignin content resulted in higher PAH emissions [41]. According to Zhang et al. [48] the atmospheric PAH values show higher trends in winter season than summer season due to increased use of biomass as a fuel.

Table 6. Toxic Equivalency of Sum of PCDD/Fs (NATO I-TEF 1988), of Sum of PCBs (WHO TEF 2006) and Sum of PCBs and PCDD/Fs in TEQ pg/Nm³. Toxic Equivalency of Sum of carcinogenic PAHs (c-PAHs) express in ng/Nm³ according to Larsen and Larsen 1998 where B(a)P factor is considered as 1.

	Punjab	AJK	Sindh
Sum PCDD/PCDF TEQ (pg/Nm3)	1493	2594	856
Sum PCB dioxin-like TEQ (pg/Nm3)	38	41	30
Sum PCDD/PCDF and PCB TEQ (pg/Nm3)	1531	2635	886
Sum c-PAH TEQ (ng/Nm3)	15353	15207	18536

TEQs of sum of dioxin (PCDD/Fs), dioxin like compounds (PCBs) and carcinogenic PAHs are shown in Table 5 collectively to express the complete but precise picture. Rice straw is proved to be a higher lignocellulosic material that proves to produce more dioxin and dioxin like compounds than less lignocellulosic agricultural waste as it inhibits the combustion conditions [49, 50]. Another prominent reason is the use of catalyst based pesticides during cropping stages. It has been estimated that the chlorinated pesticide combustion increased the dioxin and dioxin like compound concentrations by 35 to 270 folds magnitude [51, 52]. According to Tame et al. [39] and Wilhelm et al. [43] the combustion of PAH in presence of metal catalysts signify the dioxin and dioxin like compound emissions.

3.4. Emission Factors

POPs bio-accumulate and bio-magnify, so it is important to control them; although the data of chlorinated organic micropollutants are important, they take a back seat after those of c-PAHs are observed. Table 7 is the depiction of Total Emission Factor (EF) for PCDD/Fs, PCBs and PAHs from rice straw as an agricultural waste combusted in fixed grid biomass burning plant. EF is the representation of the mean POPs concentrations released per unit of activity. Total bomass burned during this study is documented in Table 4 of Supplemantary matrial while total rice crop production is documented in Table 3 of supplementay material in order to understand the extant of combustion issue. According to the data mentioned c-PAH take the lead by average 1053.6 μg TEQ/kg release followed by PCDD/Fs and PCBs. The details of the major contributing compounds resulted in this emission profile is mentioned in previous section (see 2.3). The extent of TEQ values increased with the increase in biomass uantity subject to combustion. This quantification even multiply manyfolds in subject to open burning scenario as assumed by Sormo et al. [54]. Data depicts that AJK rice straw samples declared lead in PCDD/Fs and PCBs emisisons while Sindh straw samples raised concerns with rise in c-PAHs.

Table 7. Total Emission Factor (EF) of PCDD/Fs expressed in TCDD TEQ (pg/kg), of PCBs expressed in TCDD TEQ (pg/kg), of the sum of PCDD/Fs and PCBs expressed in TCDD TEQ (pg/kg) and of carcinogenic PAHs expressed in B(a)P TEQ (μg/kg).

EF	Punjab	AJK	Sindh	Average
Sum PCDD/PCDF TEQ (pg/kg)	71.3	160.7	68.6	100.2
Sum PCB dioxin-like TEQ (pg/kg)	1.8	2.5	2.4	2.2
Sum PCDD/PCDF and PCB TEQ (pg/kg)	73.1	163.2	71	102.4
Sum c-PAH TEQ (μg/kg)	733.2	941.7	1485.8	1053.6

5. Conclusions

Biomass combustion is the most prominent cause of toxic pollutants in atmosphere. With an increase in population there is demand of increase agricultural commodities production leading to more residue wastage. Results in section 2 of this research article indicated that the combustion of agricultural residual biomass results in certain emissions resulted in an increased threat in presence with contributing catalytic factors. Bad combustion is a potential cause of c-PAHs as proved in study. In case of rice straw, the foremost factor adding to risen emissions is bad combustion due to silica, lignin and cellulose content of rice straw. Later, Cu and Fe interestingly followed by Deacon synthesis resulted in emerging PCDD/Fs, PCBs emissions. Dioxins are characterized as widespread in the air due to their stability, persistence, bio-accumulative tendencies, and lipophilic nature. They can be found globally because of long-range transport mechanisms, and the highly chlorinated PCDD/F variants tend to stay in the atmosphere since they are readily trapped by airborne particles. AJK rice straw samples, followed by Punjab and Sindh with a prevalence of 2,3,7, 8-TetraCDF and 1,2,3,7,8-PentaCDF for PCDD/Fs and same trend followed for PCBs (with 118, 105 and 167 as majority congeners) showed the same acting behaviours of major dioxin categories. As much as concern PAHs emissions, the concentrations are quite similar for all three types of straw samples which are on the order of µg/Nm^3, while Sindh taking the lead followed by Punjab and AJK. Between Zn, Fe, Cd and Cr identified by the literature as catalysts for the production of chlorinated POPs, there are no trends that identify a correspondence in the various congeners of the samples. Interestingly, however, dioxin and dl-PCBs have the same trends as identified in Cu concentrations. The emission factor analysis of total chlorinated pollutant emissions (PCDD/Fs + PCBs) showed that the largest contribution comes precisely from PCDD/Fs compared to PCBs. For this reason, the type of fertilizer/pesticide containing Cu must be chosen based on the fate of agricultural crop residues, especially if subjected to burning. Currently, the average concentrations of c-PAHs found in B(a)P TEQ for each kg of straw burned are in the hundreds of µg and considering the temporal trend of rice cultivation over the years in Pakistan. Based on the findings of current study regarding POPs emission profile, determining that there is a very high risk to human's health and surrounding environment. An alternative use of rice crop waste should be considered to eliminate the potential risk of combustion.

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