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Estimation Inventories of Persistent Organic Pollutants from Rice Straw Combustion as an Agricultural Waste

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Abstract: Rice cultivation stands as the primary agricultural activity in Asia, generating a substantial amount of agricultural waste. Unfortunately, this waste is often disposed of through burning, contributing to severe environmental, health and climate issues. This study presents the characterization of PCDD/Fs, PCBs and PAHs. The 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. Additionally, the role of agrochemicals was monitored in terms of metal catalysis resulting in POP emissions. This study provides the comprehensive characterization of the most relevant groups of pollutants (metals, PCDD/Fs, PCBs and PAHs) resulting from agricultural waste combustion. Prominent catalytic metals quantified were Cu (22–48 $\mu\text{g}/\text{Nm}^3$) and Fe (78–113 $\mu\text{g}/\text{Nm}^3$). Rice straw samples from AJK exhibited higher values of organochlorine micro-pollutants compared to those from Punjab and Sindh, i.e., $\Sigma\text{PCDD}/\text{F}$ (2594 > 1493 > 856 pg/Nm^3) and ΣPCB (41 > 38 > 30 pg/Nm^3), respectively, whereas the organic micro-pollutants $\Sigma\text{c-PAH}$, indicators of incomplete combustion (PICs), were recorded high in the samples from Sindh followed by Punjab and AJK. The average EF is 100 pg/kg , 2.2 pg/kg and 1053.6 $\mu\text{g}/\text{kg}$ for $\Sigma\text{PCDD}/\text{F}$, ΣPCB and $\Sigma\text{c-PAH}$. This study supports the idea that the phenomena leading to the formation of dioxin and dioxin-like compounds are influenced not only by poor combustion but also by the presence of metal catalysts in the burned fuel.

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



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1. Introduction

The agricultural system of paddy fields is linked to the production of massive quantities of crop waste after each harvest, including roots, stubble and straw [1]. The world annual rice crop production is 700 million tons, globally producing 80% of crop residue (2.8 billion tons) with 158 million tons of rice harvested in Asia alone [2] (632 million tons of crop residue). It is calculated that the grain-to-straw ratio varies between 0.5 and 0.7 for rice crops [3]. The common disposal method of rice straw is through open-field burnings and, in Asian countries, where this crop represents the economic pillar, this practice represents significant 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 of agricultural

residues through open burnings [6]. Currently, persistent organic pollutant (POP) emissions from biomass combustion represent significant environmental and health problems 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 the State of Azad Jammu and Kashmir (AJK) [7].

In addition to the internal sources, we must also add the contributions from the main neighbouring rice producers (such as China and India) through the transboundary movement of aerosol [8,9]. Both the local combustion and transboundary movement of aerosols contribute to local and regional air pollution. Prior to this study, the environmental conditions in Pakistan had not been subject to systematic monitoring and evaluation. Therefore, the data obtained from this investigation provide novel insights into the current situation regarding emissions of polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (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 (NO_x) 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 POPs that can be generated by bad combustion including PAHs, PCDD/Fs and PCBs [12–14].

The formation of halogenated POPs comes from the catalytic action of some metals such as the oxides of copper (Cu) and iron (Fe) [15,16]. These metals are constituent parts of the additives (pesticides, fungicides, herbicides and fertilizers) used on agricultural crops [17] (Supplementary Material Table S1) and they have been detected in biomass combustion emissions [18–20]. It must be taken into account that the agricultural additives absorbed by 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 [21]).

Studies conducted by Palma et al. [22] and Carnevale et al. [23] showed that the prominent metals emitted by combustion of agricultural residue waste include Fe, Cu, zinc (Zn), sodium (Na), magnesium (Mg), potassium (K) and calcium (Ca). Experimentation led by Mubeen et al. [24] concluded that when metals were combined with chlorine (Cl) and exposed to combustion conditions, it resulted in dioxin emissions, among which copper chloride (CuCl₂) is the major contributor in toxicity equivalent (TEQ) values. Dioxin emissions are intensifying compared to previous cultures precisely due to the application of pesticides, for example, in Hokkaido (Japan), atmospheric values have risen from 0.0058 to the existing 0.53 pg-TEQ/m³ [25]. Human exposure to atmospheric chemistry culprits is currently a major problem and is rising with every passing year. Respiratory illnesses have increased threefold in biomass combustion zones [26]. Yao et al. [27] and Zhang et al. [28] reviewed studies on PAH emissions as a result of biomass combustion and concluded that the moisture content, cellulose and lignin characterization of straw type and the emerging 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 Centre of Engineering and Agro-Food Processing (CREA-IT). Agricultural waste from the three main regions involved in rice cultivation in Pakistan (Punjab, Sindh and 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 had 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: Punjab, AJK and Sindh. Composite samples weighing 200 kg each were collected from randomly selected localities of each chosen area. Firstly, the samples were brought to Chakwal Koont agricultural farm of Pir Mehr Ali Shah Arid Agriculture University Rawalpindi for a period of one week. Later, the samples were transported to the port of Milan in Italy from the port of Karachi in Pakistan via ship cargo, where all facilities were provided for secure storage of sample. In Italy, after reaching the CNR-IIA storage facility, characteristics tests for rice straw were performed as described in Table 1.

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

2.2. Boiler and Sampling

A fixed-grid-system biomass boiler in the combustion phase, GSA 40–80 kW (D'Alessandro Termomeccanica, La Spezia, 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 powered by a mechanical system. Sampling for PCDD/Fs, PCBs and PAHs was performed according to an internal method based on EN 1948 reference methods (UNI EN 1948-1:2006, 2006; UNI EN 1948-4:2014, 2014) [29]. Sampling was conducted using an ST5 Isokinetic auto-sampler pump (DadoLab, Cinisello Balsamo, Italy) connected to a titanium probe (Isokinetic Heated Probe HP5 DadoLab, Cinisello Balsamo, Italy), which was separately used to collect both organic micro-pollutants and metals (Figure 1 and Figure 2, respectively) [30]. Briefly, PCDD/Fs, PCBs and PAHs analyses were performed using a quartz thimble containing quartz wool (Munktell, Ahlstrom-Munksjö, Helsinki, Finland) heated up to 120 ± 5 °C. The condensed vapors (6 ± 2 °C) and the gaseous fraction of samples were adsorbed on Amberlite™ XAD®-2, (Merck, Darmstadt, Germany). At the end of each sampling point, the probe was washed with 200 mL methanol (MeOH), acetone (Ace) and dichloromethane (DCM). Prior to sampling, a sampling standard solution containing isotopically labelled (¹³C) congeners of PCDD/Fs and PCBs was added to the quartz wool present in the sampling thimble.

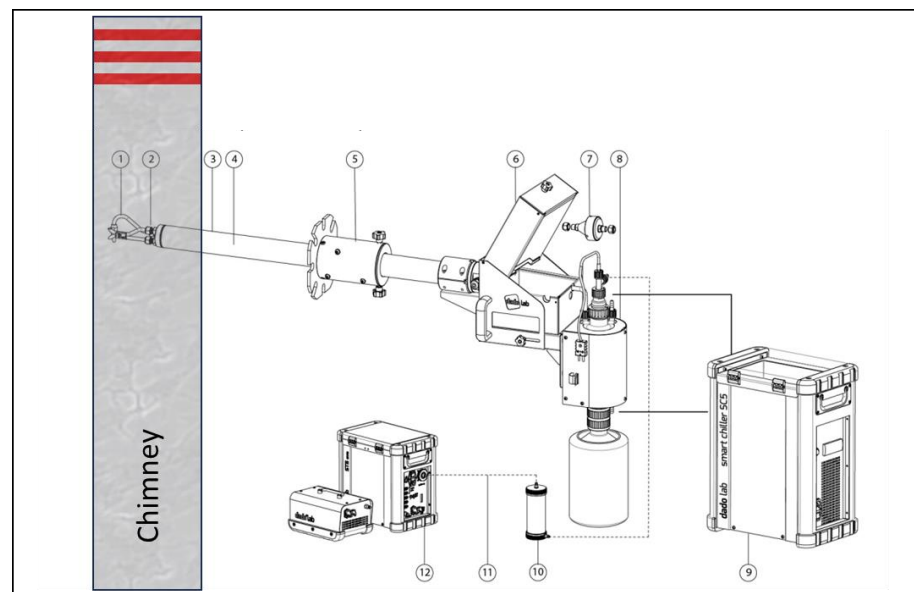


Figure 1. Schematics of sampling setup for organic micro-pollutants: Red strips: Chimney (1) gooseneck with interchangeable nozzles, (2) type S pitot tube, (3) heated probe, mod. HP5, (4) inner tube, (5) slide-and-lock device, (6) HUB for Outstack filterholder and 4DL manifold, (7) filterholder, (8) FC5 condenser for PCDDs/PCDFs, PCB and PAH, (9) SC6 Smart Chiller, (10) silica gel protection trap, (11) umbilical cable including 4TC + pitot tube + 2 thermoregulators + suction tube, (12) automatic isokinetic sampler, mod. ST5 Evo).

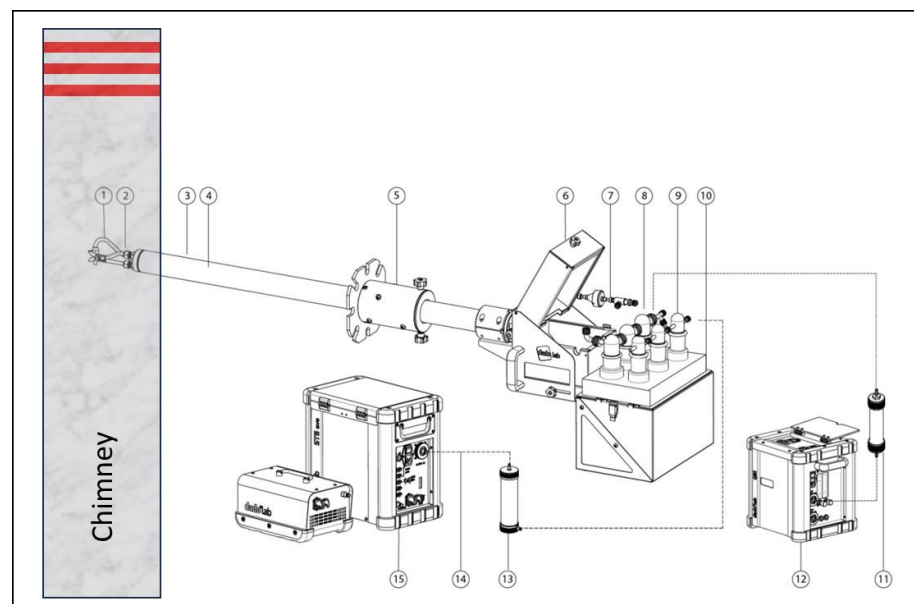


Figure 2. Schematics of sampling setup for metals: Red strips: Chimney (1) gooseneck with interchangeable nozzles, (2) type S pitot tube, (3) heated probe, mod. HP5, (4) inner tube, (5) slide-and-lock device, (6) HUB for Outstack filterholder and 4DL manifold, (7) filterholder and side sampling connector (derivation), (8) impingers train for main line (water content determination), (9) impingers train for side sampling, (10) athermal box with support foam, (11) 100 cc silica gel protection trap for side sampling line, (12) QB1 V1.5 (side sampler), (13) 1 Lt silica gel protection trap for side sampling line, (14) umbilical cable including 4TC + pitot tube + 2 thermoregulators + suction tube, (15) automatic isokinetic sampler, mod. ST5 Evo.

As for the analysis of the metals, a quartz fibre filter (QFF) (MK-360, Munktell, Värnamo, Sweden) was used and 3 bubblers were inserted downstream containing a solution of $\text{HNO}_3/\text{H}_2\text{O}_2$ (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 200 mL HNO_3 25%_{w/w} solution. The sampling was carried out between 22 November 2017 and 6 December 2017 (Supplementary Material Table S4). Each sampling point 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 perdeuterated standard solutions of PCDD/Fs, PCBs and PAHs were purchased from a local distributor of Wellington Laboratories (Guelph, ON, Canada). The sampling standard (SS) solutions contained ^{13}C -PCBs (P48-SS, 10 pg/ μL) and ^{13}C -PCDD/Fs (EN-1948SS, 10–20 pg/ μL). The extraction standard (ES) solution contained ^{13}C -labelled PCBs and PCDD/Fs (WP-LCS, 10 pg/ μL and EN-1948ES, 10–20 pg/ μL , respectively). As for PAHs, the ES solution contained perdeuterated 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 the injection standard (IS) 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, Guelph, Canada). The mixed standard solution used for ICP-MS calibration was obtained from Merck. Ace; the MeOH, toluene (Tol), DCM and n-Hexane (Hex) used in the chemical analysis were purchased from Romil (UK); the MilliQ water was from Millipore (Merck, Darmstadt, Germany); and Suprapur[®] HNO_3 65% was obtained from Merck (Merck, Darmstadt, 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, an XAD-2 cartridge, the probe condensation water and the probe wash 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 36 h with Tol after adding the ES 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 a 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, as performed by 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 triple-quadrupole gas chromatography–mass spectrometry (GC/MS) (Trace 1310 GC/TSQ 8000 Evo, Thermo Scientific, Waltham, MA, USA); the chromatographic separation was carried out on a DB-XLB column (60 m, 0.25 μm film thickness, 0.25 mm internal diameter, Agilent J&W, Santa Clara, CA, USA) using hydrogen (H_2) as the carrier gas [33].

The 1/10th of the extract dedicated to the analysis of PAHs was spiked with the ES (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 to labelled IS solution. PAHs analysis was performed on a DSQ II single-quadrupole GC/MS (Trace GC Ultra/DSQ II, Thermo, Waltham, MA, USA). The separation was performed on an Rxi@-5 ms column (30 m length with 0.25 μm film thickness, and 0.25 mm internal diameter, Restek, Centre County, PA, USA).

2.4.2. Metals

The metal 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, Sorisole, Italy). The acid attack was carried out with a solution of 6 mL of HNO₃ (65%) and 3 mL of H₂O₂ (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, VA, USA), prepared in aqueous solution acidified with 1% of HNO₃. Instrumental calibration was performed with 5 standards of increasing concentrations (from 5 to 100 ppb). Yttrium (Merck, Darmstadt, 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 (Equation (1)):

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

EF: emission factor expressed in 2,3,7,8-Tetrachlorodibenzodioxin (TCDD) TEQ pg/kg for PCDD/Fs and PCBs and in benzo[a]pyrene (B(a)P) TEQ µg/Kg for carcinogenic PAHs (c-PAH).

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 rate dry: 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. A high average ash content, represented as a percentage, indicates an elevated silica content resulting from combustion. It also enhances the bad combustion conditions in the boiler bed that inhibit the pollutant emissions [23], which is discussed in the coming sections in detail.

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 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 Cu is the one that favours the formation of organochlorine micro-pollutants, while other metals such as Zn and Cd have significantly lower catalytic activity [34]. From Table 2, it can be observed that the Cu in the AJK rice straw sample reaches $48 \pm 1 \mu\text{g}/\text{Nm}^3$, which is greater than the sample from Punjab ($35 \pm 1 \mu\text{g}/\text{Nm}^3$) and more than double compared to the rice straw samples from Sindh ($22 \pm 1 \mu\text{g}/\text{Nm}^3$). Palma et al. [30] support the same trends in relation to the 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 ($78 \pm 2 \mu\text{g}/\text{Nm}^3$) but acts as a powerful precursor due to its effective catalytic activity, along with Cu ($22\text{--}48 \mu\text{g}/\text{Nm}^3$), in the formation of PCBs and PCDD/Fs. Mg, Ca, Fe and

Zn being the top emerging metals might be a result of the irrigation water and fertilizers used for crop growth [30,35].

Table 2. Metal concentrations ($\mu\text{g}/\text{Nm}^3$) in the emissions from 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 ($\mu\text{g}/\text{Nm}^3$)	AJK ($\mu\text{g}/\text{Nm}^3$)	Sindh ($\mu\text{g}/\text{Nm}^3$)
Mg	321 \pm 7	611 \pm 10	691 \pm 10
Al	82 \pm 2	53 \pm 2	98 \pm 2
Ca	362 \pm 7	486 \pm 9	370 \pm 7
Cr	4.9 \pm 0.1	2.2 \pm 0.1	4.3 \pm 0.1
Mn	18.3 \pm 0.4	30.4 \pm 0.6	32.9 \pm 0.7
Fe	113 \pm 2	78 \pm 2	106 \pm 2
Co	1.3 \pm 0.1	0.1 \pm 0.1	0.2 \pm 0.1
Ni	11.1 \pm 0.3	9.9 \pm 0.3	6.2 \pm 0.2
Cu	35 \pm 1	48 \pm 1	22 \pm 1
Zn	134 \pm 3	89 \pm 2	93 \pm 2
Sr	4.9 \pm 0.2	22.2 \pm 0.5	16.6 \pm 0.4
Ag	0.1 \pm 0.1	0.1 \pm 0.1	0.2 \pm 0.1
Cd	0.9 \pm 0.1	0.8 \pm 0.1	0.4 \pm 0.1
Ba	1.9 \pm 0.1	4.4 \pm 0.1	3.8 \pm 0.1
Tl	0.1 \pm 0.1	0.1 \pm 0.1	0.1 \pm 0.1
Pb	13.5 \pm 0.3	14.5 \pm 0.3	14.4 \pm 0.3
Bi	4 \pm 0.1	7.2 \pm 0.1	8.8 \pm 0.2

3.3. PCDD/Fs, PCBs and PAHs

Rice straw has a high silica content (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%), with the latter known as a lingo-cellulosic biomass [37,38]. 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 the three rice straw samples. The distribution of the 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. As observed from Table 1, the macro-constituents of the fuels appear to be similar. The PCDD/F 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 emissions.

In the three rice straw samples, there is a clear dominance of OctaCDD, 2,3,7,8 TetraCDF and 1,2,3,7,8 PentaCDF compared to other congeners. The sum PCDD/Fs TEQ is higher in the AJK rice straw sample followed by the Punjab and Sindh samples. OCDD represents the lead emission, depicting a highly stable and persistent PCDD congener. It is formed as an impurity in products of chlorine chemistry, such as chlorophenols, which are among the main starting products of the chlorinated pesticides used in agriculture [40]. But a significantly higher emission of 2,3,7,8 TetraCDF is observed from the Punjab sample, of 964 pg/Nm^3 . It is followed by the emissions of 1,2,3,7,8 PentaCDF, recorded as 642 pg/Nm^3 (AJK), and 1,2,3,7,8 PentaCDF, noted as 465 pg/Nm^3 .

All values were correlated with the International Toxicity Equivalency Factor (I-TEFs) NATO 1988 recommendation index for TEF. Based on the results, these three compounds potentially contributed to the total PCDD/F findings. The combustion conditions were supported by the addition of metals as catalysts (Cu or Fe) [23], or were inhibited, as in the case of rice straw, due to the high silica and lignocellulose content [41]. The literature

also supports the fact that thermal decomposition of lignocellulose material favours the formation of phenols, resulting in the precursor route of dioxin formations [42].

Table 3. PCDD/F concentrations (in pg/Nm³ and pg TEQ/Nm³) and their TEQs for rice straw samples in reference to International Toxicity Equivalency Factors (I-TEFs NATO 1988).

Compound	Punjab			AJK		Sindh	
	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	28,722	28.71	127,646	127.64	26,675	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	12,833	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		51,037	1492.82	158,795	2593.97	37,424	856.44

The data from Table 4 reveal an interesting phenomenon for PCDD/Fs. The significantly higher sum PCB data revealed by AJK rice straw samples (41 dl-TEQ pg/Nm³), followed by Punjab (38 dl-TEQ pg/Nm³) and Sindh (30 dl-TEQ pg/Nm³), likely contribute to the sum PCDD/Fs concentrations. This is based on a consideration of the PCB values detected in the three straw samples in relation to TEFs articulated by World Health Organization (WHO) 2006 guidelines (Table 4). Table 4 is quite revealing in several ways as it can be noticed that the highest TEQ was emitted by 2,3',4,4',5-PentaCB, attributed to both its abundance in the intentionally produced industrial mixtures and its high persistence in the environment among all the dl-PCBs. As reported by Kaya et al. [43], 2,3',4,4',5-PentaCB is the most abundant dioxin-like congener among the PCB congeners of Aroclor 1254, accounting for, on average, 7% to 13.5% by weight depending on the production lot. According to the sales record of Monsanto U.S., the world's biggest PCB producer, between 1957 and 1974 Aroclor 1254 was the second most produced/sold Aroclor mixture after Aroclor 1242. Moreover, it is one of the most persistent dioxin-like congeners in the environment, while 3,3',4,4',5-PentaCB was present at 38 pg/ Nm³ (AJK), followed by 35 pg/ Nm³ (Punjab) and 26 pg/ Nm³ (Sindh). Interestingly, the highest collective emissions emerged from the Sindh rice straw samples (87,255 pg /Nm³), but TEQs conflict this trend and AJK (41 dl-TEQ pg/Nm³) shows a rise as a result. This might be the reason for the highest results being obtained for 3,3',4,4',5-PentaCB and its highest WHO-TEF.

Chlorinated compounds originating from pesticides or fertilizers were believed to be responsible for dioxin emissions resulting from combustion [22,30,44]. These compounds are normally not specifically associated with combustion. In fact, they are found mostly in ambient air samples and especially in urban areas [45]. We observed higher dioxin emissions than those reported in the literature for PCBs [30], which was assumed to be due to poor combustion conditions during the rice straw experiment [46]. Several scientific pieces of evidence demonstrate how chlorine acts as a catalyst during combustion in the Deacon synthesis process for the formation of chlorinated compounds [47,48]. Cu mainly derives from the fungicide treatments to which the rice crop is subjected at various stages

of growth. As listed in the Supplementary Materials, more than one fungicide contains the metal Cu, i.e., copper oxychloride and cuprous oxide, and it is also present in a mixture of products such as Bordeaux and Moltovin (see Supplementary Material Table S1).

Table 4. PCB amounts in pg and concentrations in toxicity equivalent (TEQ pg/Nm³) of Punjab, AJK and Sindh rice straw samples.

Compounds	WHO TEF 2006	Punjab		AJK		Sindh	
		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-TetraCB	0.0003	153	0.046	340	0.1021	263	0.0790
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	29,258	0.878	33,910	1.0172	44,926	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	10,292	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	16,046	0.481	23,623	0.7086	30,071	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		61,991		76,867		87,255	
∑PCB dioxin-likeTEQ			38		41		30

The concentrations of PAHs compared to those of PCDD/Fs and PCBs are significantly higher (Table 5). Fourteen PAHs were quantified during the current study including carcinogenic compounds (benzo(a)anthracene, benzo(b+j)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 the European Council (2004). Sum PAHs were considerably higher in Sindh (18,536 ng/Nm³) followed by Punjab (15,353 ng/Nm³) and AJK (15,207 ng/Nm³) rice straw samples. Benzo(a)pyrene had the highest TEF value [49], which is also a contributing factor to the highest values from straw samples that ranged between 6779 and 10,327 ng/Nm³, dominated by Sindh, having greater toxicity threats. These values are directly expressed as TEQ itself. Therefore, having the highest TEF, it is the compound that represented most of the total concentration of PAHs in the individual experiments of rice straw combustion.

In the Sindh samples, a trend of a rise in fluranthene by 3398 ng/Nm³ followed by dibenzo(a,h)anthracene (1787–2285 ng/Nm³) was observed. Moisture percentage, metal catalysts and high lignin content resulted in higher PAH emissions [42]. According to Zhang et al. [50], atmospheric PAH values show higher trends in the winter season than the summer season due to the increased use of biomass as a fuel.

The TEQs of sum of dioxin (PCDD/Fs), dioxin-like compounds (PCBs) and carcinogenic PAHs are collectively presented in Table 6 to express a complete but precise picture. Rice straw is proven to be a higher lignocellulosic material that produces more dioxin and dioxin-like compounds than lignocellulosic agricultural waste, as it inhibits combustion conditions [51,52]. Another prominent reason is the use of catalyst-based pesticides during cropping stages. It has been estimated that the combustion of chlorinated pesticides increased the concentrations of dioxin and dioxin-like compounds 35- to 270-fold [53,54]. According to Tame et al. [39] and Wilhelm et al. [43], the combustion of PAH in the presence of metal catalysts results in the emission of dioxin and dioxin-like compounds.

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

Compounds	TEF	Punjab (ng/Nm ³)	AJK (ng/Nm ³)	Sindh (ng/Nm ³)
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	10,327
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		15,353	15,207	18,536

Table 6. Toxic equivalency of sum of PCDD/Fs (NATO I-TEF 1988), 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) expressed in ng/Nm³ according to Larsen and Larsen 1998, where B(a)P factor is considered as 1.

	Punjab	AJK	Sindh
Sum PCDD/PCDF (pg TEQ /Nm ³)	1493	2594	856
Sum PCB dioxin-like (pg TEQ /Nm ³)	38	41	30
Sum PCDD/PCDF and PCB (pg TEQ /Nm ³)	1531	2635	886
Sum c-PAH (ng TEQ /Nm ³)	15,353	15,207	18,536

3.4. Emission Factors

POPs bioaccumulate and biomagnify, so controlling them is important; although the data on chlorinated organic micropollutants are essential, they take a back seat to those of c-PAHs. Table 7 depicts the total emission factor (EF) for PCDD/Fs, PCBs and PAHs from rice straw as an agricultural waste combusted in a fixed-grid biomass burning plant. EF represents the mean POP concentrations released per unit of activity. The total biomass burned during this study is documented in Table S4 of the Supplementary Materials, while the total rice crop production is documented in Table S3 of the Supplementary Materials to understand the extent of the combustion issue.

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

According to the mentioned data, c-PAH takes the lead with an average of 1053.6 µg TEQ/kg released, followed by PCDD/Fs and PCBs. The details of the major contributing compounds in this emission profile are mentioned in the previous section (see Section 2.3). The extent of TEQ values increased with the increase in the biomass quantity subjected to combustion. This quantification multiplies manifold in the case of an open-burning

scenario, as assumed by Sormo et al. [55]. The data depict that the AJK rice straw samples were in the lead in PCDD/F and PCB emissions, while the Sindh straw samples raised concerns with the rise in c-PAHs.

4. Conclusions

Biomass combustion stands out as the most prominent cause of toxic pollutants in the atmosphere. With an increase in population there is a demand for increased agricultural commodity production, leading to more residue wastage. The results in Section 2 of this research article indicate that the combustion of agricultural residual biomass results in certain emissions, leading to an increased threat with contributing catalytic factors. Bad combustion is a potential cause of c-PAHs, as proven in this study. In case of rice straw, the foremost factor contributing to increased emissions is bad combustion due to the silica, lignin and cellulose content of rice straw. Later, Cu and Fe, interestingly followed by Deacon synthesis, resulted in emerging PCDD/F and PCB emissions. Dioxins are characterized as widespread in the air due to their stability, persistence, bioaccumulative 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 samples, with a prevalence of 2,3,7, 8-TetraCDF and 1,2,3,7,8-PentaCDF for PCDD/Fs and following the same trend for PCBs (with 118, 105 and 167 as majority congeners), showed the same activity as major dioxin categories. In terms of PAH emissions, the concentrations are quite similar for all three types of straw samples, which are on the order of $\mu\text{g}/\text{Nm}^3$, while the Sindh samples take the lead, followed by the Punjab and AJK samples. Between Zn, Fe, Cd and Cr identified in 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 those 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 micrograms, and this is important considering the temporal trend of rice cultivation over the years in Pakistan. Based on the findings of the current study regarding the POP emission profile, it can be determined that there is a very high risk to human health and the surrounding environment. An alternative use of rice crop waste should be considered to eliminate the potential risk of combustion.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/fire6120459/s1>. Table S1: Rice crop spray used in Pakistan (© 2021 Syngenta PAKISTAN—Rice, 2021). Table S2: Wheat crop spray used in Pakistan (© 2021 Syngenta PAKISTAN—Wheat, 2021). Table S3: Statistics of total area of Rice cultivation, Rice crop production and yield from past 5 years in Pakistan (Pakistan Bureau of Statistics (Government of Pakistan). Pakistan Economy Survey 2019–2020, 2020). Table S4: Details of Metals and POPs (PCDD/fs, PCBs and PAHs) samplings. Tav Stack: Average temperature in the stack ($^{\circ}\text{C}$); Biomass feeding: kg of biomass burned per hour (kg/h).

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Abbreviations

Abbreviations	Explanation
Ace	Acetone
AJK	Azad Jammu Kashmir
BC	Black carbon
C	Carbon
Ca	Calcium
CEN	European Committee for Standardization
Cl	Chlorine
CNR-IIA	National Research Council of Italy, Institute of Atmospheric Pollution Research
c-PAH	Carcinogenic Polycyclic aromatic hydrocarbons
CREA-IT	Council for Agricultural Research and Economics, Center of Engineering and Agro-Food Processing
Cu	Copper
DCM	Dichloromethane
EF	Emission factors
ES	Extraction standard
Fe	Iron
GC/MS	Gas chromatography/mass spectroscopy
H	Hydrogen
H ₂ O ₂	Hydrogen peroxide
Hex	Hexane
HNO ₃	Nitric acid
ICP-MS	Inductively coupled plasma mass spectrometry
IS	Injection standards
ISO	International Standard Organization
I-TEF	International Toxicity Equivalent Factor
K	Potassium
Kg/h	Kilogram per hour
MeOH	Methanol
Mg	Magnesium
N	Nitrogen
Na	Sodium
Na ₂ SO ₄	Sodium sulphate
NaCl	Sodium chloride
NATO	North Atlantic Treaty Organization
O ₂	Oxygen
PAH	Poly aromatic hydrocarbon
PCB	Poly chlorinated biphenyls
PCDDs	Polychlorinated dibenzodioxins
PCDFs	Polychlorinated fibenzofurans

pg/Nm ³	Pico gram per normal cubic metre
PICs	Products of incomplete combustion
PM	Particulate matter
POPs	Persistent organic pollutants
ppb	Parts per billion
QFF	Quartz fibre filter
S	Sulphur
SS	Sampling standard
TCDD	2,3,7,8-Tetrachlorodibenzo-p-dioxin
TEQ	Toxicity equivalent quotient
Tol	Toluene
USEPA	United States Environmental Protection Agency
WHO	World Health Organization
XAD-2	Amberlite styrene-divinylbenzene (macroreticular)
Zn	Zinc

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