



Chemical composition of indoor ash residues

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Original Article

Abstract

The ash content formed after burning of materials in indoor may be harmful to environment on dumping due to high ionic and metallic concentration. Therefore, the chemical composition of various indoor ash residues derived from burning of the biomass (BM), coal (C), cow dung (CD), incense (IS) and mosquito coil (MC) materials is described in this study. Three samples each of BM, coal, CD, IS and MC materials were burnt. The ash residues were collected and sieved out the particles of mesh size ≤ 0.1 mm size. The Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} , Ca^{2+} content ($n = 15$) was ranged from 0.12-8.27, 0.01-0.64, 0.74-12.53, 0.06-4.47, 0.29-15.45, 0.30-2.51 and 0.68-19.05% with mean value of 1.81 ± 1.18 , 0.10 ± 0.08 , 3.31 ± 1.66 , 1.05 ± 0.70 , 4.92 ± 2.04 , 1.27 ± 0.36 and $7.68 \pm 2.94\%$, respectively. The composition of metals, that is, Fe, Cr, Mn, Ni, Cu, Zn and Pb ($n = 15$) was ranged from 1100-24,600, 12-211, 109-1102, 5-142, 21-145, 25-244 and 5-42 mg/kg with mean value of 95 ± 31 , 474 ± 152 , 43 ± 23 , 75 ± 23 , 107 ± 32 and 16 ± 6 mg/kg, respectively. The enrichment and fluxes of ions and metals of indoor ash residues are described.

KEYWORDS: Ash Residue, Biomass, Coal, Cow Dung, Incense, Ions, Metals, Mosquito Coil

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Introduction

Indoor particulate matter (PM) air pollution is being several folds more dangerous than the outdoor particulate air pollution in developing countries like India due to widespread use of solid fuels [i.e., wood, charcoal, coal, cow dung (CD), crop residues, etc.] for purposes, that is, cooking, heating, etc., The combustion of these materials generates aerosol particles as well as high content of ash in the coarse (PM_{10}), fine ($\text{PM}_{2.5}$) and ultrafine ($\text{PM}_{0.1}$) mode having a very complex chemical composition with high potential environmental and health risks.¹ In the developing countries, that is, China, India and Sub-Saharan Africa, about 80% households still use solid fuels such as wood, coal, CD and crop residues as an

energy source.² The incense (IS) and mosquito coil (MC) materials are used to fragrance and to repel mosquitoes in indoor environments, respectively. The particulate emitted during burning causes several health problems.^{3,4}

Wood ash is formed after combustion of wood that can be related to coal ash, which is a fossilized wood.⁵ The study reported that all the major compounds present in wood ash were present in coal ash.⁶ The elements, that is, silica, Al, Ca, Fe, K, Mg, Na, P, Si, Ti, As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Tl, V, Zn, etc. are main constituents of the ash.^{7,8} The wood and coal ash components cause several environmental and health effects, that is, deposit formation, aerosol emissions, corrosion, disposal of ashes, increase in pH, ion composition on the surface of the vegetation and on the upper soil horizon, organ disease, cancer, respiratory illness, neurological

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damage, developmental problems, and even kill plants and animals, and etc.⁹⁻¹¹

The composition of metals in some ash residues, that is, biomass (BM) and coal has already been reported.¹²⁻²² However, as far as the authors are aware of, this is the first time that the ions and metal composition in BM and coal (C), CD, IS and mosquito coil (MC) ash residues derived from indoor burning is being studied in Raipur, Chhattisgarh, India. The obtained results may be used to predict the future health hazards.

Materials and Methods

Fifteen materials (i.e., three samples of each BM, coal, CD, IS and MC materials) were burnt over a clean granite sheet in an indoor environment, (a room of $0.5 \times 0.5 \text{ m}^2$). The cold ash residue was collected in a polyethylene bag by using a plastic spoon. The ash samples were sieved to particles with mesh size $\leq 0.1 \text{ mm}$. They were dried for overnight at 60°C in an oven. A 5.0 g of ash samples were used for ions extraction with 50 ml of deionized water for overnight in a 250 ml plastic conical flask. The ash was extracted with aqua regia in closed plastic vessels in the microwave accelerated reaction system 5 microwave digestion system.²³ The extracted samples were used for the analysis of metals.

The Ion Chromatograph (DX120, Dionex, USA) equipped with anion separation column (AS9-HC, $250 \times 4 \text{ mm}$), cation separation column (CS12A, $25 \times 04 \text{ mm}$) and conductivity detector was used for analysis of the ions. The eluents, 9 mm Na_2CO_3 (1.4 ml/min) and 20 mm methanesulfonic (0.8 ml/min) were used for leaching of the anion and cation, respectively. Standards (AR, E. Merck) were used for preparation of the calibration curves to evaluate the soluble ion content in the samples. Blank and replicate analyses were performed for 10% of all samples according to standard operating procedures. Method detection limits (MDL) of ionic species (in $\mu\text{g/ml}$) were Cl^- (0.044), NO_3^- (0.077), SO_4^{2-} (0.046), Na^+ (0.091), K^+ (0.123), Mg^{2+} (0.007), Ca^{2+} (0.143). Laboratory blanks were

used to assess contamination. The blank compositions of ionic species were less than corresponding MDLs. Compositions of non-detects were taken as zero. In this study, ND indicates that the value is below the level of detection limitation.

The Varian liberty AX sequential inductively coupled plasma-atomic emission spectroscopy and varian AA280FS atomic absorption spectrophotometer equipped VGA-77 (plasma flow: 15 l/min, an auxiliary flow: 1.5 l/min, power: 1 kw, PMT voltage: 650 V) were used for analysis of the metals in the indoor ash residues. The detection limit of the instrument was $2 \mu\text{g/l}$ with percentage recovery of 102.5 at $80 \mu\text{g/l}$. The 5% HCl/0.5% HNO_3 solution served as both the blank solution and the rinse solution.

The weighted amount of materials, that is, BM, coal (C), CD, IS and MC were burnt over a clean granite sheet. After complete burning, the cold ash residues were collected and weighted out. The ash content of the materials was calculated. The composition of the ions and metals was determined by using appropriate techniques. The flux of the species was measured using the following equation:

Flux of chemical species in materials = $(\text{Composition in ash} \times \text{Ash\% in a given material})/100$

Results and Discussion

Composition of ions and metals in indoor ash residues

The compositions of ions and metals in the ash residues are presented in tables 1 and 2. The Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} and Ca^{2+} composition in the ash residues ($n = 15$) was ranged from 0.12-8.27, 0.01-0.64, 0.74-12.53, 0.06-4.47, 0.29-15.45, 0.30-2.51 and 0.68-19.05% with the mean values of 1.81 ± 1.18 , 0.10 ± 0.08 , 3.31 ± 1.66 , 1.05 ± 0.70 , 4.92 ± 2.04 , 1.27 ± 0.36 and $7.68 \pm 2.94\%$, respectively. The ions, that is, Cl^- , Mg^{2+} and Ca^{2+} showed the highest composition in the BM ash residue, as they are inherently present in the BM. Whereas, the highest

Table 1. Composition of ions in indoor ash residues (%)

Samples	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
BM ₁	1.70	0.03	2.44	2.34	6.09	2.09	13.96
BM ₂	8.27	0.03	4.49	1.13	4.12	2.43	10.75
BM ₃	6.14	0.04	5.95	1.43	7.63	1.12	12.32
C ₁	0.26	0.07	0.74	0.06	0.32	0.30	0.68
C ₂	0.31	0.08	0.89	0.07	0.38	0.36	0.82
C ₃	0.29	0.09	0.78	0.06	0.29	0.34	0.78
CD ₁	1.08	0.01	1.90	0.15	3.54	0.99	3.38
CD ₂	1.40	0.01	2.47	0.20	4.60	1.29	4.39
CD ₃	1.54	0.02	2.72	0.21	5.06	1.42	4.83
IS ₁	0.25	0.10	1.05	0.12	2.90	1.90	19.05
IS ₂	0.12	0.03	1.56	0.11	1.00	0.84	3.30
IS ₃	0.54	0.04	12.53	0.51	15.45	0.79	10.84
MC ₁	2.20	0.64	8.08	1.25	5.90	1.23	15.65
MC ₂	2.04	0.17	2.18	4.47	7.76	2.51	7.25
MC ₃	1.07	0.14	1.90	3.57	8.75	1.51	7.21

The experiment was performed 3 times and its results are presented in detail: 1; Experiment 1, 2; Experiment 2, 3; Experiment 3; BM: Biomass; C: Coal; CD: Cow dung; IS: Incense; MC: Mosquito coil

Table 2. Composition of metals in indoor ash residues (mg/kg)

Samples	Fe	Cr	Mn	Ni	Cu	Zn	Pb
BM ₁	8600	177	365	18	144	244	11
BM ₂	1100	12	145	85	24	98	5
BM ₃	2600	42	522	33	145	144	19
C ₁	2900	164	202	101	76	25	29
C ₂	3500	191	240	118	91	29	35
C ₃	3300	211	278	142	109	35	42
CD ₁	15700	57	848	17	21	80	6
CD ₂	20400	74	981	23	27	104	8
CD ₃	22500	81	1102	25	30	108	9
IS ₁	14100	50	109	5	50	48	8
IS ₂	24600	51	562	26	29	72	10
IS ₃	6300	91	288	15	64	156	16
MC ₁	14600	37	445	23	59	118	33
MC ₂	21200	96	476	11	133	170	10
MC ₃	16800	85	552	9	119	177	5

The experiment was performed 3 times and its results are presented in detail: 1; Experiment 1, 2; Experiment 2, 3; Experiment 3; BM: Biomass; C: Coal; CD: Cow dung; IS: Incense; MC: Mosquito coil

composition for other three ions, that is, NO₃⁻, Na⁺ and K⁺ was marked in the MC ash residue, may be due to addition of their salts as ingredients (Figure 1).

The mean composition of anions (i.e., Cl⁻, NO₃⁻ and SO₄²⁻) in the BM, C, CD, IS and MC was observed to be 1.20%, 3.73%, 5.43% and 6.48%, respectively. The lowest composition of the anions was seen in the coal ash residue, may be due to their removal from the coal by the weathering. Compared with cations, the

composition of anions in the CD ash residue was reduced to half. High composition of anions was observed in three ash residues, that is, BM, IS and MC. The highest composition of Cl⁻ and SO₄²⁻ was marked in the BM ash residue. Whereas, the composition of Cl⁻ was remarkably suppressed in the IS ash residue. The highest composition of NO₃⁻ was marked in the MC ash residue, may be due to mixing of nitrate salt as ingredients in the MC during the preparation. The increased anionic composition in ash

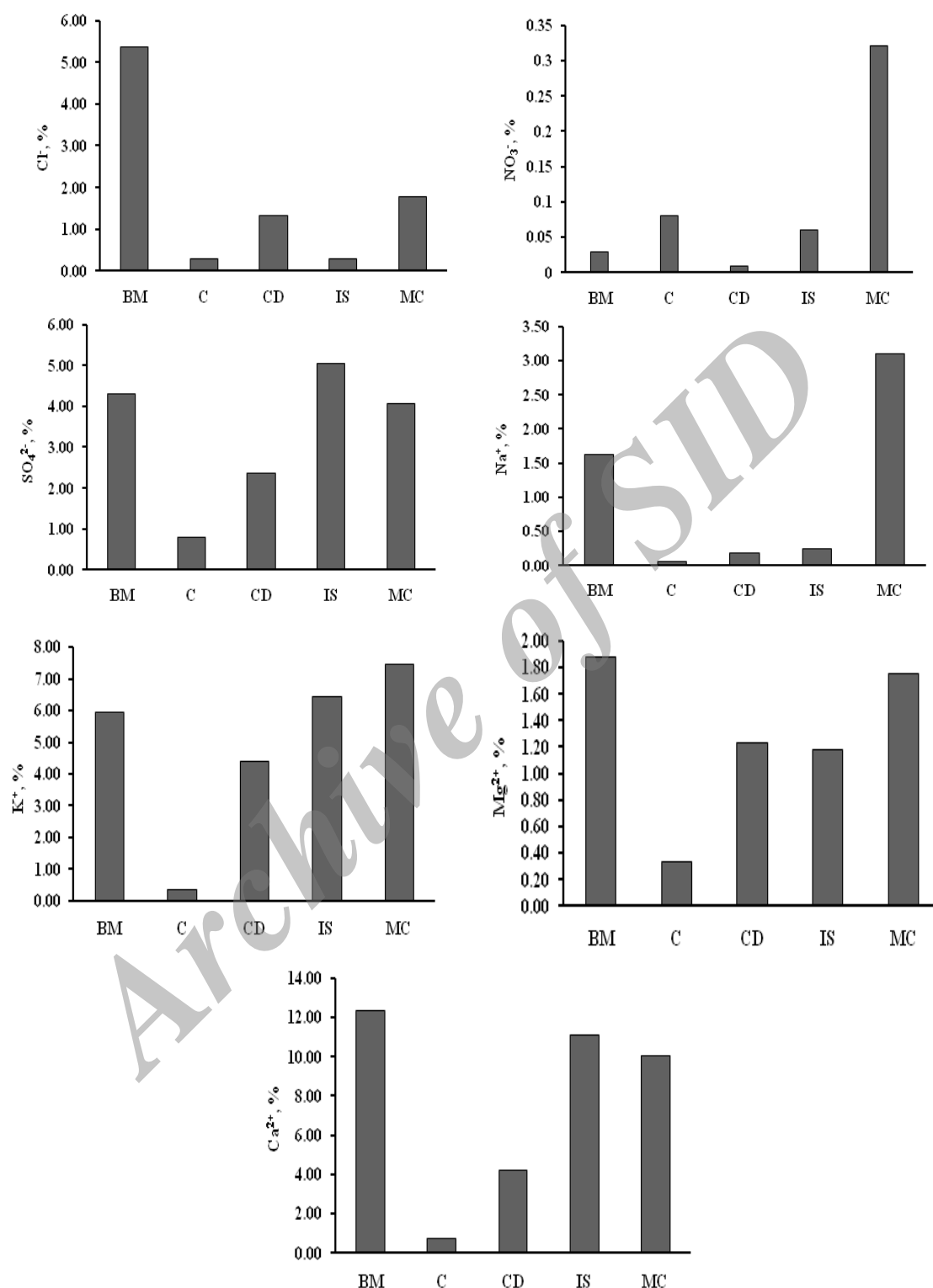


Figure 1. Mean composition of ions: Cl^- , NO_3^- , SO_4^{2-} , Na^+ , K^+ , Mg^{2+} and Ca^{2+} in ash residues, that is, biomass, coal, cow dung, incense and mosquito coil
 BM: Biomass; C: Coal; CD: Cow dung; IS: Incense; MC: Mosquito coil

residues affects the soil fertility on their disposal in surface. Relatively higher composition of cations (i.e., Na^+ , K^+ , Mg^{2+} and Ca^{2+}) was observed in all ash residues, and their mean ranged from 1.48% to 22.36%. Their lowest composition was marked in the coal ash residue, may be due to their removal from the coal by the weathering. The composition of the cations in the CD ash residue was reduced at least 50% to the BM content, may be due to their sorption in the animal body from the raw food. The highest composition of the cations was observed in the BM and MC ash residues may be due to their accumulation from the soil or addition as ingredients.

The composition order of ions for the studied ash residues was as follows:

BM: $\text{Ca}^{2+} > \text{K}^+ > \text{Cl}^- > \text{SO}_4^{2-} > (\text{Na}^+, \text{Mg}^{2+}) > \text{NO}_3^-$;
 C (coal): $(\text{SO}_4^{2-}, \text{Ca}^{2+}) > (\text{Cl}^-, \text{K}^+, \text{Mg}^{2+}) > (\text{NO}_3^-, \text{Na}^+)$;
 CD: $\text{K}^+ > \text{Ca}^{2+} > \text{SO}_4^{2-} > \text{Cl}^- > \text{Mg}^{2+} > \text{Na}^+ > \text{NO}_3^-$;
 IS: $\text{Ca}^{2+} > \text{K}^+ > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{NO}_3^-$;
 and MC: $\text{Ca}^{2+} > \text{K}^+ > \text{SO}_4^{2-} > \text{Na}^+ > (\text{Mg}^{2+}, \text{Cl}^-) > \text{NO}_3^-$. Ca^{2+} , K^+ were the predominant ions in all ash residues, because plant is the base material for all of them. NO_3^- was marked as the ion with the lowest concentration in all ash residues. In general, potassium element is found as a tracer of BM burning.^{24,25} However in this study, we have observed Ca^{2+} ion in a higher level. Campbell,²⁶ and Ohno and Susan Erich,²⁷ were also found calcium as the most abundant element had a mean of almost 20% of the ash. When compared to calcium, other nutrients in BM ash were about 4% potassium, and < 2% phosphorus, magnesium, aluminum and sodium. They found the mean value of elements in decreasing order as calcium, potassium, magnesium, sodium in wood ash. These mean values were from 12 different wood ashes, that is, six from Maine and six from other states. The limited composition of ions in ash residues make them useful for soil and human health.

Similarly, the composition ($n = 15$) of metal, that is, Fe, Cr, Mn, Ni, Cu, Zn and Pb was ranged from 1100 to 24600, 12-211, 109-1102, 5-142, 21-145, 25-244 and 5-42 mg/kg with mean value of 11880 ± 4177 , 95 ± 31 , 474 ± 152 , 43 ± 23 ,

75 ± 23 , 107 ± 32 and 16 ± 6 mg/kg, respectively. Among metals in indoor ash residues, iron showed strongly dominated in the all the ash residues. Whereas, Cu and Zn exhibited the highest composition in the BM ash residue, because they are micronutrients presented in plants. The increased composition of Cu and Zn has also been shown in wood and/or bark of young Norway spruce.²⁸ Other metals, that is, Cr, Ni and Pb showed the highest composition in the coal ash residue. These three metals are found to be harmful to plants as well as human beings. Nickel carcinogenicity has been reported in both animals and man. Increased values of Ni can cause alteration of the activity of some certain enzymes and also it can suppress immunity. Cr can be source of illnesses, that is, prolonged allergic dermatitis and potentially carcinogenicity. In general, Cr accumulates in the lung, kidney, liver, spleen. A high level of Cr, therefore, causes serious some adverse effects in these organs, especially in lungs.^{29,30} The increased level of Pb affects the nervous system, hemoglobin formation by interfering enzymatic activities and even every organ system. Thus, presence of such toxic metals in coal ash residue can cause harmful effect, when they mixed with air or disposed in the soil. The higher composition of Fe and Mn in the CD ash residue may be due to their lower sorption in the animal body from the raw food (Figure 2).

Enrichment of ions and metals

The BM and coal are natural solid fuel. The CD is a biodegraded fuel. Whereas, the IS MC are the synthetic fuming material. Upon burning, majority of volatile elements are emitted out, and the non-volatile elements remained in the ash residues. The enrichment of ions and metals was evaluated in the various ash residues with respect to the BM ash residue; the result shows the different level of metals due to different burning conditions (Table 3). The nitrate was strongly enriched (> 10-folds) in the MC ash residue with respect to the BM ash may be due to mixing of their salts as ingredients in the MC

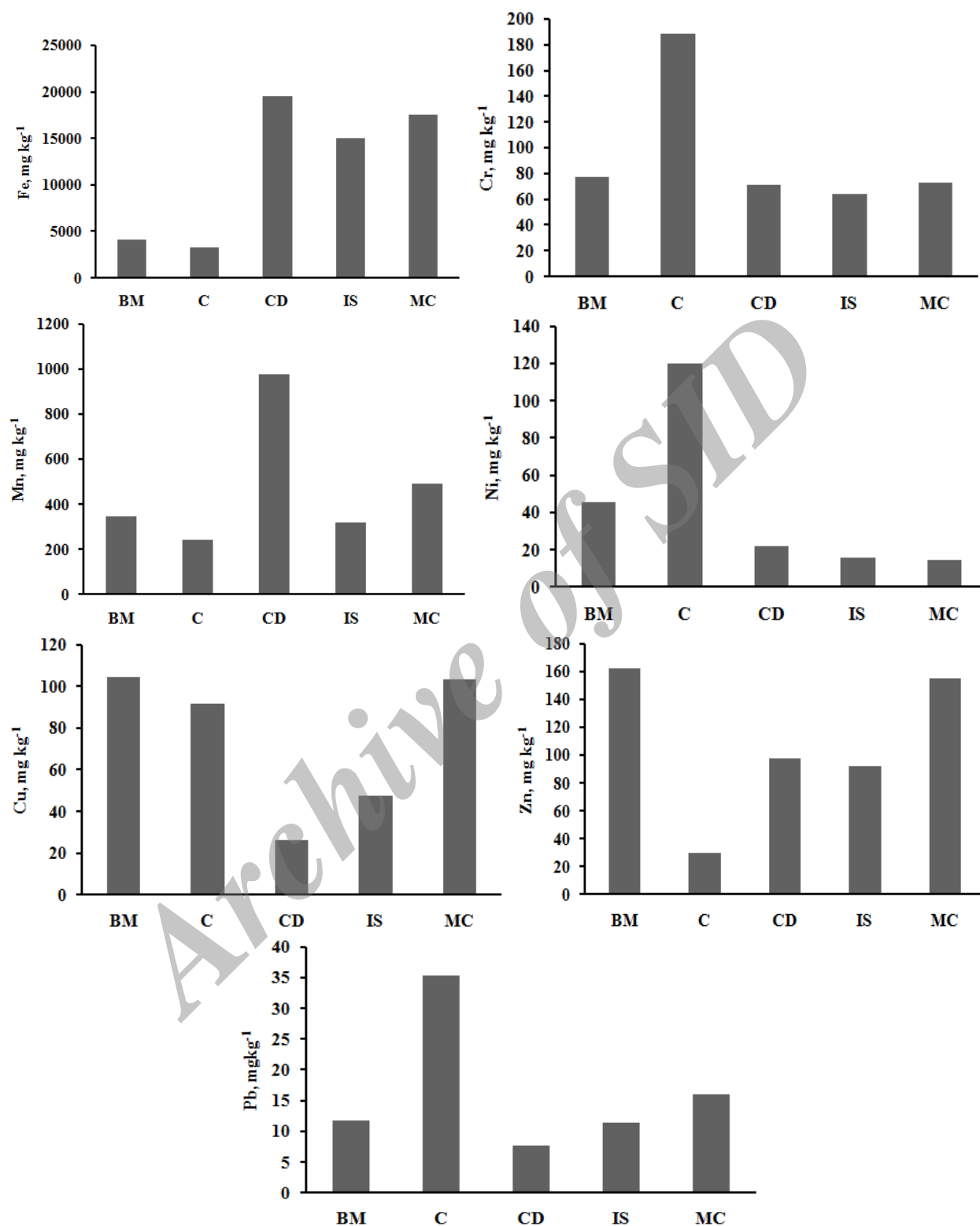


Figure 2. Mean composition of metals: Fe, Cr, Mn, Ni, Cu, Zn and Pb in ash residues, that is, biomass, coal, cow dung, incense and mosquito coil
 BM: Biomass; C: Coal; CD: Cow dung; IS: Incense; MC: Mosquito coil

Table 3. Enrichment of ions and metals in the indoor ash residues with respect to the BM ash content

Ions	C	CD	IS	MC
F ⁻	1.10	0.60	0.70	13.70
Cl ⁻	0.10	0.30	0.10	0.30
NO ₃ ⁻	2.70	0.40	1.90	10.60
SO ₄ ²⁻	0.20	0.60	1.20	0.90
Na ⁺	0.00	0.10	0.20	1.90
K ⁺	0.10	0.70	1.10	1.30
Mg ²⁺	0.20	0.70	0.60	0.90
Ca ²⁺	0.10	0.30	0.90	0.80
Fe	0.80	4.80	3.70	4.30
Cr	2.50	0.90	0.80	0.90
Mn	0.70	2.80	0.90	1.40
Ni	2.70	0.50	0.30	0.30
Cu	0.90	0.30	0.50	1.00
Zn	0.20	0.60	0.60	1.00
Pb	2.90	0.60	0.90	1.30

BM: Biomass; C: Coal; CD: Cow dung; IS: Incense; MC: Mosquito coil

during the manufacturing time. Similarly, the higher level of Fe was found in CD, IS and MC. Whereas, the metal, that is, Cr, Ni, and Pb in coal and Cu and Zn in MC were marked in higher level. Similarly, existed Mn in CD and MC was higher than the other ash residues. The metals show no definite order in all ash residues.

Fluxes of ions and metals

The fluxes of the chemical species depend on two factors: their composition in the ash and ash percentage of the materials. The fluxes of ions

and metals was evaluated in the materials that is, BM, C (coal), CD, IS and MC (Tables 4 and 5). Among five burnt materials, the CD produced the highest content of ash, 46.9%. Therefore, the highest fluxes of ions, that is, Cl⁻, SO₄²⁻, K⁺, Mg²⁺, Ca²⁺ and metals were observed with the CD. However, the highest fluxes of NO₃⁻ and Na⁺ were marked with the MC ash residue.

Comparison of metals with other reported studies

As the best of our knowledge, the composition of metals in CD, IS and MC was not reported yet. The metal composition in wood and coal ash residues reported in different studies is summarized in table 6. The composition of metals, that is, Fe, Cr, Mn, Ni, Cu, Zn and Pb in the ash residues of the present work is found to be comparable with the previous reported wood and coal ash residues. Among all metals, in the present work, compared to other studies, higher composition of Fe and Mn in all ash residues was found.¹²⁻¹⁴ In this study, the toxic metals, that is, Ni, Cr and Pb in coal ash residues were marked in higher level that is consistent with reported works.^{16,18} Higher composition of toxic metals, in coal ash residue, make it more harmful for environment than the other tested ash residues. The Cu and Zn were found in higher level in BM.

Table 4. Fluxes of ions in indoor ash residues (g/kg)

Samples	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
BM ₁	1.36	0.02	1.95	1.87	4.87	1.67	11.17
BM ₂	4.14	0.02	2.25	0.57	2.06	1.22	5.38
BM ₃	4.30	0.03	4.17	1.00	5.34	0.78	8.62
C ₁	0.26	0.07	0.74	0.06	0.32	0.30	0.68
C ₂	0.25	0.06	0.71	0.06	0.30	0.29	0.66
C ₃	0.26	0.08	0.70	0.05	0.26	0.31	0.70
CD ₁	5.62	0.05	9.88	0.78	18.41	5.15	17.58
CD ₂	6.02	0.04	10.62	0.86	19.78	5.55	18.88
CD ₃	7.08	0.09	12.51	0.97	23.28	6.53	22.22
IS ₁	0.25	0.10	1.05	0.12	2.90	1.90	19.05
IS ₂	0.06	0.02	0.78	0.06	0.50	0.42	1.65
IS ₃	0.43	0.03	10.02	0.41	12.36	0.63	8.67
MC ₁	1.98	0.58	7.27	1.13	5.31	1.11	14.09
MC ₂	1.22	0.10	1.31	2.68	4.66	1.51	4.35
MC ₃	0.86	0.11	1.52	2.86	7.00	1.21	5.77

The experiment was performed 3 times and its results are presented in detail: 1; Experiment 1, 2; Experiment 2, 3; Experiment 3; BM: Biomass; C: Coal; CD: Cow dung; IS: Incense; MC: Mosquito coil

Table 5. Fluxes of metals in indoor ash residues (mg/kg)

Samples	Fe	Cr	Mn	Ni	Cu	Zn	Pb*
BM ₁	688	14	29	1	12	20	880
BM ₂	55	1	7	4	1	5	250
BM ₃	182	3	37	2	10	10	1330
C ₁	290	16	20	10	8	3	2900
C ₂	280	15	19	9	7	2	2800
C ₃	297	19	25	13	10	3	3780
CD ₁	8164	30	441	9	11	42	3120
CD ₂	8772	32	422	10	12	45	3440
CD ₃	10350	37	507	12	14	50	4140
IS ₁	1410	5	11	1	5	5	800
IS ₂	1230	3	28	1	1	4	500
IS ₃	504	7	23	1	5	12	1280
MC ₁	1314	3	40	2	5	11	2970
MC ₂	1272	6	29	1	8	10	600
MC ₃	1344	7	44	1	10	14	400

The experiment was performed 3 times and its results are presented in detail: 1; Experiment 1, 2; Experiment 2, 3; Experiment 3; * $\mu\text{g/kg}$, BM: Biomass; C: Coal; CD: Cow dung; IS: Incense; MC: Mosquito coil

Table 6. Comparison of metals in ash residues in various studies

S. No.	Ash type	Composition (mg/kg)							Reference
		Fe	Cr	Mn	Ni	Cu	Zn	Pb	
1	Wood	5000-20000	10-250	1000-30000	6-200	15-300	15-2200	15-650	12
2	Wood	2500	22	8200	18	108	675	32	13
3	Wood	3600	80	9000	38	184	935	45	14
4	Wood	-	-	-	-	84.8	3860	-	30
5	Coal	-	204.0-218.2	-	-	135.6-252.0	87.5-155.3	427.9-551.3	16
6	Coal	-	64	-	41	38	120	44	18
7	BM	1100-8600	12-177	145-522	18-85	24-145	98-244	5-19	Present work
8	Coal	2900-3500	164-211	202-278	101-142	91-109	25-35	29-42	
9	CD	15700-22500	57-81	848-1102	17-25	21-30	80-108	6-9	
10	IS	6300-24600	50-91	109-562	5-15	29-64	48-156	8-16	
11	MC	14600-21200	37-96	445-552	9-23	59-133	118-177	5-33	

BM: Biomass; C: Coal; CD: Cow dung; IS: Incense; MC: Mosquito coil

Conclusion

The highest composition of anions (i.e., Cl^- , NO_3^- and SO_4^{2-}) was observed in three ash residues, that is, BM, IS and MC, showing that their disposal can acidify the soil and affect its fertility, which is also harmful for human life. The MC ash residue was relatively enriched with a high content of NO_3^- , Na^+ and K^+ ions due to mixing of their salt (i.e., sodium benzoate and potassium nitrate) as an ingredient during making. The highest composition of cations (i.e., Na^+ , K^+ , Mg^{2+} and Ca^{2+}) was marked in BM and

MC ash residues may be due to their accumulation from the soil and addition as ingredients, respectively.

Similarly, the high composition of toxic metal, that is, Ni, Cr and Pb was found in coal ash residue than others, showing higher toxicity of coal ash residue. The coal ash residue may harmful for living beings. Different orders of metal composition were marked in the ash residues. The highest fluxes were marked with CD, showing that it is also a major contributor of toxic metals and create harmful effect in plants and human beings.

Conflict of Interests

Authors have no conflict of interests.

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