SUPPLEMENTARY MATERIAL

PCDD/F Formation in Milled Fly Ash: Metal Chloride Catalysis

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Table S.1 Short and elementary analysis of activated carbon and silica (SiO_2).

Activated Carbon (wt.%)														
Elements	C	H	O	N	S	Zn	Cu	Pb	Mn	Si	Ti	Fe	Cr	Ca
	93	1.5	1.7	0.2	0.2	0.0	0.0	0.0	0.2	1.5	2.7	3.4	0.4	1.1

Moisture	Ash	Volatiles	Fixed carbon
1.7	2.1	7.4	89

Silica (wt.%)							
Elements	Zn	Cu	Ca	Mn	Mg	Ni	Fe	Cr
	n.d.	n.d.	0.2	n.d.	0.1	0.0	0.0	0.0

S.1 Characteristics of original materials

The activated carbon powder was first washed with distilled water and acetone, respectively, and then completely dried for about 4 h at 100 °C. The silica powder of 100-200 mesh size (purity > 99%) was rinsed with distilled water and then dried for about 4 h at 100 °C.

The metal species used in the tests were $CuCl_2$•$2H_2O$ (99%), $CrCl_3$•$6H_2O$ (AR), $FeCl_3$ (anhydrous, AR) $ZnCl_2$ (PT, Primary reagent) and $CaCl_2$ (anhydrous) (AR). Aladdin Chemistry Co. Ltd. supplied all metal compounds.

S.2 Milling of MFA

An all-dimensional planetary ball mill (QXQM-2, Changsha Tencan Powder Technology Co., Ltd, China) was used for the milling treatment (Fig. S1).Compared with the conventional planetary ball mill, this unit adds a dimension of rotation. The disk and four pots slowly rotate (1 rpm) around main spindle to avoid sedimentation of materials caused by gravity, making powders to be ground more completely. The milling pots, with volume of 500 mL, and balls with either 8 or 12 mm diameter were made of stainless steel, weighing 2.1 g or 7.1 g, respectively. Samples of about 40 g fly ash were charged into each pot, together with an equal weight of big (10) and small balls (43), with a ball to powder ratio of 4 wt. /wt. The mill was operated for 2 and 16 h (1 and 8 h milling), with a 30-min driving belt cooling interval every 30 min. The rotation speed of the disk was set at 300 rpm and the rotational direction

changed automatically every 30 min. After MC treatment, milled fly ash (MFA) was collected for further analysis.

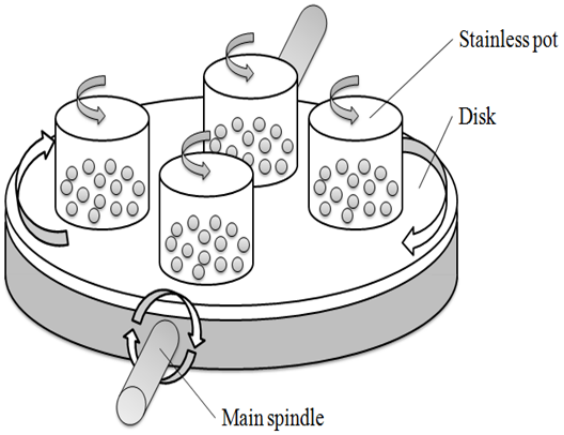

Fig. S.1 Schematic representation of an all-dimensional planetary ball mill.

S.3 Clean-up and analysis of PCDD/F

Gas phase (XAD-2 resin, toluene, and adsorbed condensate) and solid phase (fly ash residue) samples were Soxhlet-extracted with toluene for 24 h. Before Soxhlet extraction the sample was spiked with 10 µL EPA1613-LCS standards. Then the extract was concentrated to 1-2 mL with a rotary evaporator and diluted with hexane to 10 mL. After adding 25 µL1613-ISS clean up internal standard, half of the concentrated solution went to sample clean-up including a multi-silica gel column and a basic-alumina column, while the other half was kept at 4 °C for possible reworking of the pre-treatment. The eluate was blown by nitrogen and kept at 4 °C after adding 1613-ISS standards and waited for analyses.

All analyses were performed by means of High Resolution Chromatography with a DB-5MS column (60 m × 0.25 mm × 0.25µm) coupled with High Resolution Mass Spectrometry (JMS-800D, JEOL, Japan). The temperature program for GC oven was as follows: initial temperature 75 °C, held for 2 min; 75-150 °C at15 °C min^{-1}; 150–290 °C at 2.5 °C min^{-1}, then held for 1 min. Carrier gas, helium (99.999 %), 1.2 ml min^{-1}. The isotope standards were purchased from Cambridge Isotope Laboratories. The target compounds were all tetra- to octa-CDD/F as well as the seventeen 2, 3, 7, 8-substituted PCDD/F.

S.4 Composition of MFA samples

Table S.2 reports on the Composition of MFA samples (XRF analysis) doped with 0.2 wt. % selected metals at 0, 1 and 8 h milling treatment. A comparison of this composition suggests:

- The extent of experimental error and variability between the values for the successive conditions of the MFA.
- The considerable increase of Fe, Cr, Ni and Mn, after 1 h (+13.8, +16.7, +16.9, +16.4, +17.7%) and 8 h (6.3%, 4.2%, 4.8%, 4.2%, 4.0%). This increase is due to attrition of the

steel elements during milling.

- Sum elements may give rise to volatile compounds. These are C, S, Cl and (as chlorides) Na, K, Cu…

Table S.2 Composition of MFA samples (XRF analysis) doped with 0.2 wt. % selected metals at 0, 1 and 8 h milling treatment.

	$CuCl_2$			$CrCl_3$			$FeCl_3$			$ZnCl_2$			$CaCl_2$		
Elements	**0h**	**1h**	**8h**	**0h**	**1h**	**8h**	**0h**	**1h**	**8h**	**0h**	**1h**	**8h**	**0h**	**1h**	**8h**
Ca	0.4	0.0	0.0	0.2	0.0	0.0	0.1	0.0	0.0	0.5	0.0	0.0	0.8	0.1	0.2
Si	40.4	36.4	35.0	33.6	25.9	32.3	40.5	26.6	32.3	43.6	26.3	32.1	41.8	26.4	32.9
Al	0.1	0.2	0.2	0.4	0.1	0.1	0.3	0.1	0.1	0.0	0.1	0.1	0.3	0.1	0.2
Cl	7.6	6.8	9.0	8.1	6.9	8.7	5.3	6.5	8.7	7.3	6.8	8.6	4.3	6.0	8.1
Mg	0.0	0.0	0.0	0.2	0.0	0.1	0.1	0.1	0.1	0.8	0.1	0.1	0.1	0.0	0.1
Fe	0.4	12.5	3.8	0.5	12.7	3.8	0.7	12.6	3.8	0.5	12.2	3.6	0.4	12.9	3.2
Na	11.2	7.6	10.3	8.9	8.2	10.2	4.0	7.8	10.2	11.4	8.6	10.8	2.1	7.7	10.3
Ti	0.6	0.0	0.3	0.4	0.1	0.2	0.3	0.1	0.2	0.1	0.2	0.2	0.4	0.2	0.2
Zn	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.2	0.1	0.1	0.0	0.0	0.0
Cu	0.2	0.2	0.2	0.0	0.2	0.0	0.0	0.2	n.d.	0.0	0.2	0.0	0.0	0.2	0.0
Mn	0.0	0.8	1.2	0.0	2.6	0.7	0.0	2.4	0.7	0.0	2.4	0.6	0.0	2.7	0.6
S	0.0	0.0	0.0	n.d.	0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.0
Cr	0.1	1.0	1.8	0.7	2.4	0.8	0.1	2.4	0.7	0.1	2.2	0.6	0.1	2.4	0.6
K	n.d	n.d	n.d	0.1	0.0	n.d.	0.1	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0
Ni	n.d	n.d	n.d	0.0	0.2	0.1	n.d.	0.3	0.1	0.1	0.3	0.1	0.0	0.2	0.1
Cd	n.d	n.d	n.d	n.d.	0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Co	n.d	n.d	n.d	n.d.	0.0	0.0	n.d.	0.0	0.0	0.0	0.0	0.0	n.d.	0.0	0.0
Fe+Cr+Ni+Mn Sum	0.5	14.3	6.8	1.2	17.9	5.4	0.8	17.7	5.3	0.7	17.1	4.9	0.5	18.2	4.5

n.d.= not detected below 0.1%

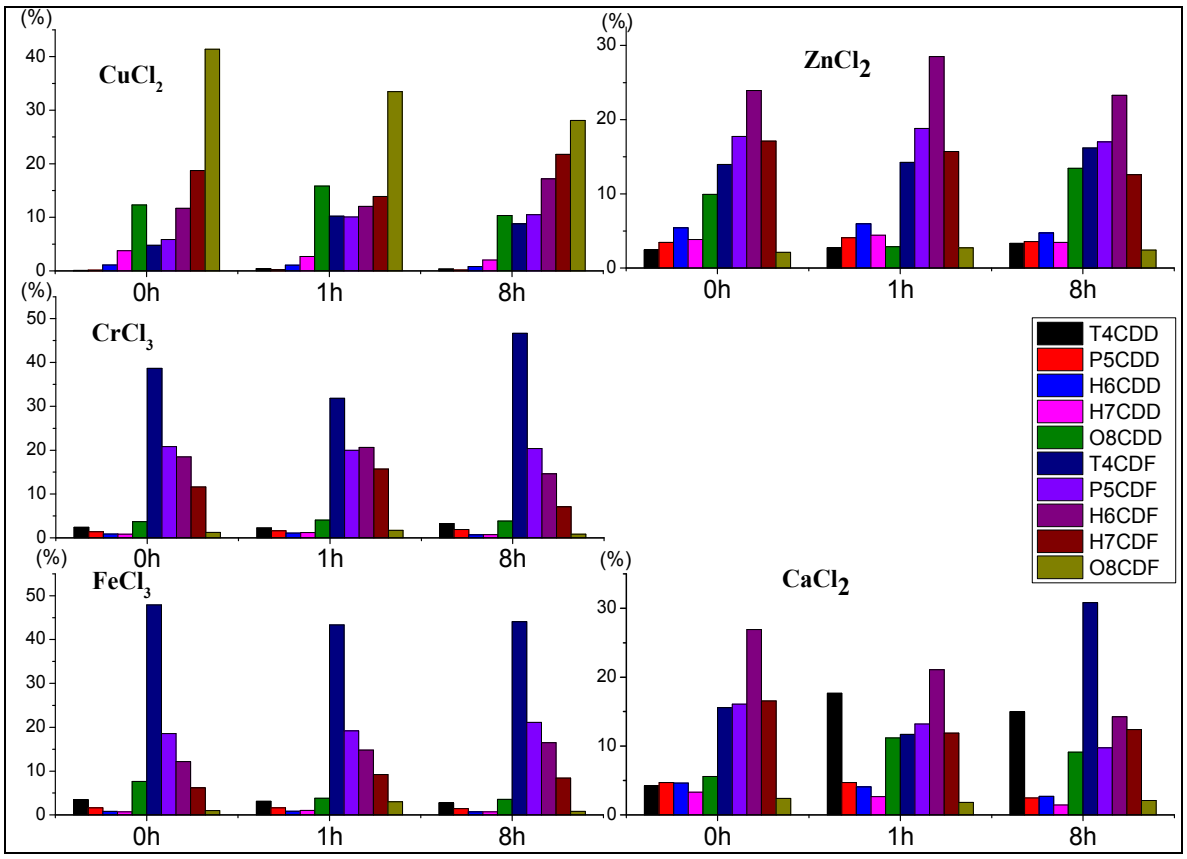

Fig S.2 All PCDD/F homologue profiles of metal doped MFA, milled at 0, 1 and 8h.

Table S.3 Maximum, Minimum and average isomer percentages of 2,3,7,8-PCDD/F for MFA samples.

	$CuCl_2$			$CrCl_3$			$FeCl_3$			$ZnCl_2$			$CaCl_2$		
	Min.	**Max.**	**Ave.**	**Min.**	**Max.**	**Ave.**	**Min.**	**Max.**	**Ave.**	**Min.**	**Max.**	**Ave.**	**Min.**	**Max.**	**Ave.**
2378	2.6	3.3	3.0	2.1	2.3	2.2	2.4	2.9	2.6	2.2	2.9	2.5	1.9	3.7	2.7
12378	4.0	4.9	4.4	5.6	6.3	6.0	5.6	6.5	6.1	9.0	9.6	9.3	2.2	14.3	8.7
123478	2.9	3.6	3.2	7.3	9.0	7.9	7.8	8.2	8.1	4.9	5.5	5.2	4.5	4.7	4.6
123678	5.5	7.7	6.8	6.7	8.2	7.3	8.2	8.9	8.5	8.3	10.3	9.0	7.9	10.5	8.9
123789	8.0	9.4	8.8	3.7	4.3	4.0	4.1	5.7	4.9	6.5	6.7	6.6	5.4	6.7	6.3
1234678	47.8	49.2	48.6	38.6	42.0	40.2	36.2	46.1	41.0	45.4	47.7	46.8	46.4	51.7	48.3
2378	6.4	8.8	7.3	6.2	7.2	6.6	6.0	6.6	6.4	4.2	4.8	4.4	2.5	4.6	3.8
12378	2.7	4.0	3.3	2.5	3.1	2.9	2.9	3.1	3.0	5.2	5.6	5.4	5.1	7.1	6.0
23478+	9.2	10.2	9.7	5.6	7.0	6.4	6.7	7.6	7.1	10.6	11.2	10.8	11.5	15.0	13.4
123478	6.9	8.2	7.3	7.3	8.0	7.6	7.1	8.0	7.6	11.1	11.6	11.3	10.6	12.7	11.4
123678	6.5	8.2	7.3	5.6	6.8	6.1	6.4	6.6	6.5	10.4	11.1	10.8	10.7	11.8	11.1
234678+	16.2	17.6	16.8	7.3	8.3	7.7	7.6	10.7	9.0	12.3	14.3	13.1	11.7	14.2	13.1
123789+	4.9.	6.0	5.4	1.3	1.5	1.4	1.2	2.7	1.8	2.6	2.7	2.6	2.4	2.5	2.4
1234678	46.6	50.4	48.5	84.2	85.6	85.0	70.7	85.7	79.7	55.7	58.5	57.3	56.9	70.1	62.4
1234789	9.8	10.1	9.9	1.8	2.9	2.2	1.6	5.5	3.8	0.0	0.0	0.0	7.5	16.3	10.8

Table S.4 2,3,7,8-PCDD/F (pg WHO-TEQ g^{-1} MFA) contributions to the WHO-TEQ values for MFA samples milled at 0, 1 and 8 h

Time,h	$CuCl_2$			$CrCl_3$			$FeCl_3$			$ZnCl_2$			$CaCl_2$		
	0h	**1h**	**8h**	**0h**	**1h**	**8h**	**0h**	**1h**	**8h**	**0h**	**1h**	**8h**	**0h**	**1h**	**8h**
2378	63	31	7	4.98	5.79	4.89	2.65	6.03	4.58	1.18	1.61	1.20	0.85	4.38	2.84
12378	606	103	19	8.75	11.34	7.15	2.36	8.35	6.63	6.57	7.63	5.23	5.38	6.03	0.27
123478	129	14	3	0.66	0.87	0.43	0.18	0.55	0.41	0.59	0.64	0.37	0.17	0.26	0.06
123678	285	23	4	0.60	0.86	0.39	0.18	0.59	0.44	1.11	1.01	0.66	0.30	0.43	0.15
123789	362	30	7	0.39	0.47	0.18	0.13	0.29	0.24	0.71	0.81	0.51	0.20	0.36	0.09
1234678	864	45	8	0.34	0.52	0.20	0.06	0.39	0.19	0.35	0.43	0.27	0.14	0.17	0.03
12346789	130	16	2	0.11	0.14	0.08	0.06	0.09	0.08	0.06	0.02	0.07	0.01	0.04	0.01
2378	166	46	8	8.20	6.60	6.55	2.97	7.69	6.23	1.82	1.48	1.18	0.88	0.96	3.43
12378	116	25	5	1.79	1.73	1.29	0.46	1.41	1.29	1.60	0.63	0.47	0.23	0.31	0.11
23478+	3673	940	182	34.88	43.91	28.90	11.05	33.22	30.10	11.16	12.93	8.89	6.08	6.06	2.24
123478	2216	294	91	13.70	17.06	7.93	2.56	8.58	8.91	5.35	6.46	4.39	2.28	3.06	0.92
123678	2132	297	89	10.98	13.09	6.72	2.04	7.92	7.51	4.96	6.47	4.15	2.28	3.08	0.86
234678+	5648	723	159	13.96	17.06	8.14	2.75	12.82	8.92	6.78	7.36	4.68	3.04	3.74	0.85
123789+	1682	190	57	2.41	3.24	1.50	0.46	3.21	1.42	1.30	1.50	0.97	0.52	0.68	0.18
1234678	2351	271	101	9.89	15.16	4.02	1.34	5.28	5.10	1.58	1.87	1.18	0.75	0.96	0.44
1234789	530	36	12	0.23	0.32	0.14	0.07	0.41	0.10	0.25	0.29	0.20	0.21	0.14	0.05
12346789	200	35	7	0.04	0.06	0.02	0.01	0.07	0.02	0.01	0.02	0.01	0.01	0.01	0.00
2,3,7,8-PCDD/F	**21154**	**3122**	**762**	**111.90**	**138.19**	**78.52**	**29.31**	**96.91**	**82.16**	**45.37**	**51.15**	**34.42**	**23.33**	**30.67**	**12.55**

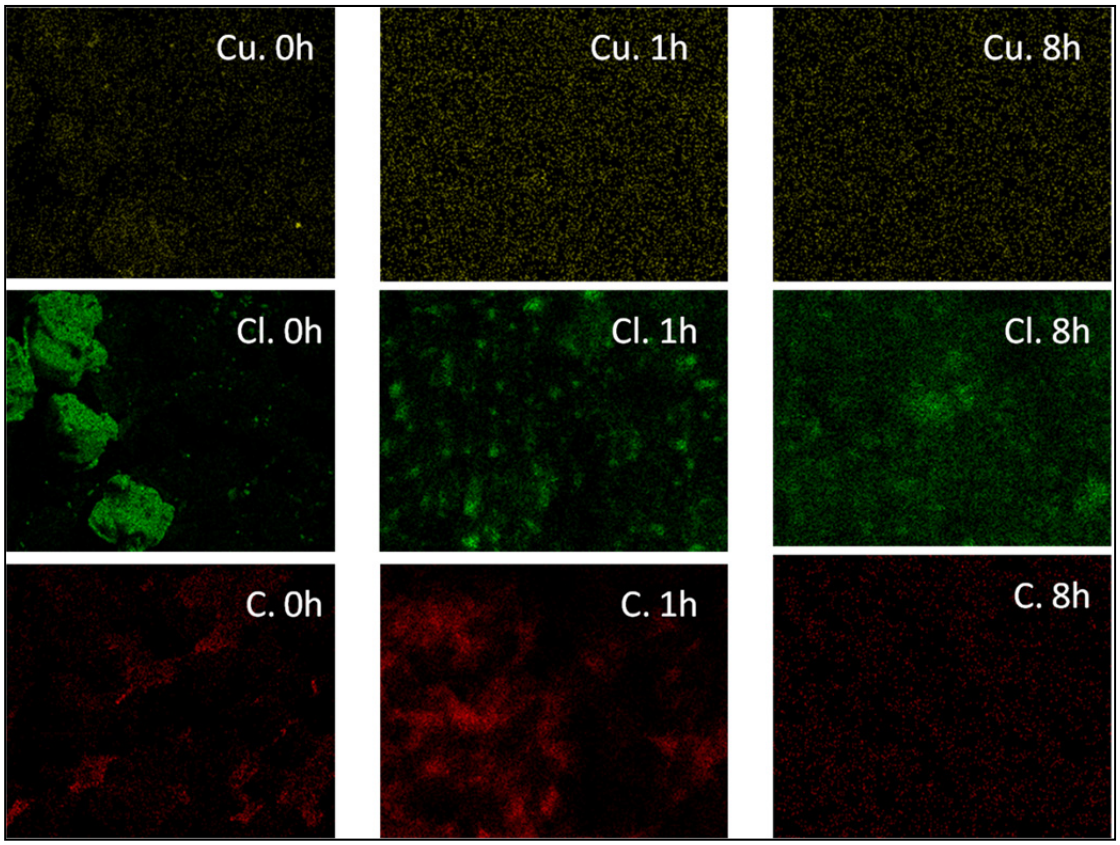

Fig. S.3 Match between the key elements (C, Cu and Cl) with different milling times for Cu doped MFA, derived from SEM/EDX mapping magnified at ×1000 (1k) (detailed maps for other elemnets are included in our next paper).

Table S.5 Percent isomer distributions of PCDD/F in 0, 1 and 8 h milled MFA samples.

	$CuCl_2$			$CrCl_3$			$FeCl_3$			$ZnCl_2$			$CaCl_2$		
Time, h	**0h**	**1h**	**8h**	**0h**	**1h**	**8h**	**0h**	**1h**	**8h**	**0h**	**1h**	**8h**	**0h**	**1h**	**8h**
1368	13	16	24	15	13	15	18	18	13	23	27	32	35	6	16
1379	7	10	17	9	7	9	10	10	7	17	14	17	22	4	9
1369	3	2	1	3	3	4	3	4	4	4	4	3	2	1	1
1469	1	0	1	1	0	1	0	1	2	2	0	1	1	1	0
1247+	15	12	11	16	17	15	15	14	16	6	8	7	7	10	4
1378	7	7	6	7	7	7	7	7	7	8	8	8	4	7	8
1268	5	5	4	5	5	5	4	5	5	2	3	3	2	10	7
1478	2	3	2	2	2	2	1	2	1	1	1	1	2	10	10
1279	8	8	5	6	5	5	5	5	5	4	3	3	4	15	6
1234+	12	14	5	5	7	4	4	5	6	2	4	4	2	15	14
1236	4	1	5	5	5	5	5	4	4	2	2	1	6	6	6
1237+	9	8	8	12	12	12	12	11	13	8	9	9	3	4	3
1239	3	5	2	3	4	3	3	3	4	2	1	1	3	5	4
2378	3	2	2	2	2	2	3	2	2	2	3	2	3	2	4

1278	5	4	3	5	6	6	5	5	6	4	4	3	1	1	2
1267	2	2	2	3	3	3	2	2	2	1	1	0	1	1	1
1289	2	1	1	2	2	2	2	2	2	10	8	6	2	1	6
12479+	21	22	19	19	17	16	19	20	17	21	23	23	19	5	32
12469	13	10	10	6	6	21	6	5	6	4	4	4	4	6	5
12368	13	15	13	11	10	11	12	13	11	19	18	18	12	17	19
12478	4	5	5	6	6	4	6	6	6	8	8	7	4	5	3
12379	8	10	10	9	8	8	9	10	10	12	11	12	9	12	10
12369+	9	6	11	16	16	13	13	14	16	10	11	9	7	6	0
12347+	9	12	10	15	17	11	15	15	15	7	7	10	7	6	10
12378	16	12	13	6	6	6	6	6	7	10	9	9	14	10	2
12367	4	5	5	7	7	6	7	7	7	6	5	4	11	3	2
12389	4	4	4	5	6	5	6	5	6	3	4	4	12	30	16
124679+	11	10	12	13	14	14	9	12	14	11	14	14	13	12	9
123468	37	41	31	28	23	27	29	28	23	28	26	28	32	28	46
123679+	23	21	24	22	22	20	21	22	21	30	31	31	30	33	17
123469	2	2	3	6	7	6	8	5	6	4	3	3	3	4	3
123478	3	4	5	7	7	9	8	8	8	6	5	5	5	5	4
123678	7	6	7	7	7	8	8	8	9	10	8	9	8	8	11
123467	7	7	8	14	15	13	11	13	13	5	5	5	4	4	3
123789	9	8	11	4	4	4	6	4	5	7	7	7	5	7	7
1234679	52	52	53	60	61	58	64	54	59	55	52	53	48	54	53
1234678	48	48	47	40	39	42	36	46	41	45	48	47	52	46	47
1368	1	1	1	2	2	3	3	3	2	4	4	4	4	5	2
1468	1	1	1	2	2	2	2	2	2	2	2	2	2	3	1
2468	1	1	1	2	2	2	3	2	2	3	2	3	3	4	2
1247+	9	9	11	15	15	15	15	14	16	12	13	13	10	13	5
1367+	5	4	5	8	8	8	9	8	8	8	9	8	7	9	3
1268	3	2	2	3	3	3	3	3	3	3	3	3	3	4	2
1467	2	2	3	3	3	3	3	3	3	2	2	2	2	1	0
1478	1	1	1	2	2	2	2	2	2	3	3	3	2	2	1
1369+	9	8	8	8	8	8	8	9	8	8	8	8	8	8	3
2467	2	2	2	3	3	3	4	3	3	3	3	4	3	2	2
1238+	25	23	19	15	16	15	14	15	15	8	9	9	10	8	6
1278+	4	4	4	4	4	4	4	4	4	11	8	7	11	8	31
1267	4	4	3	4	4	3	4	3	4	3	4	3	4	3	7
2348	4	4	3	5	5	6	5	6	3	2	2	3	3	2	1
2378	2	1	1	2	2	2	2	2	2	5	5	4	7	6	22
2347+	9	5	5	5	5	4	4	4	5	4	5	4	2	4	1
2346+	6	11	10	6	7	6	6	7	7	4	4	5	5	4	3
2367+	9	14	15	9	9	8	8	9	9	12	12	12	11	10	1
1269	1	1	1	1	1	1	1	1	1	1	1	1	1	2	9
1239	1	1	1	0	0	0	1	1	0	1	1	1	1	1	0
1289	1	1	1	0	0	0	1	0	0	1	1	0	1	0	0

13468+	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
13678+	11	13	16	18	18	18	18	18	19	14	16	16	15	16	12
12368+	6	8	8	10	9	10	11	10	10	22	18	18	16	16	24
14678	3	3	5	6	5	6	5	5	6	3	4	4	4	5	3
13479	0	1	1	1	1	1	1	1	1	2	2	1	1	2	1
12479+	1	2	3	2	2	2	2	2	2	2	2	2	2	2	1
12346	14	17	15	18	19	17	17	17	18	8	9	9	9	10	7
23468+	8	4	4	6	7	6	6	6	6	3	3	4	3	4	2
12348	6	4	4	6	6	5	5	5	5	3	3	3	2	3	2
12378	3	2	2	3	3	3	3	3	3	5	6	6	5	6	7
12367+	11	11	10	10	10	10	11	10	10	10	10	10	9	10	15
12379	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
12679	1	1	1	3	1	1	1	1	1	1	1	1	1	1	1
12369+	20	20	18	10	11	11	10	13	10	14	14	14	13	13	8
23478+	10	9	7	6	6	7	8	7	7	11	11	11	14	11	15
12349	3	3	2	1	1	1	1	1	1	1	1	1	3	1	1
12389	1	1	1	0	0	0	1	0	0	1	1	1	1	0	1
123468	8	8	9	16	16	15	14	13	15	8	8	9	8	8	8
134678	19	22	26	29	27	28	28	25	29	26	29	28	29	29	32
134679	1	2	3	2	2	2	2	2	2	3	3	3	3	3	2
124679	3	3	4	2	2	2	2	3	2	4	4	4	3	4	3
124689	1	1	2	1	1	1	1	1	1	2	2	2	2	2	2
123467	23	19	19	25	27	23	24	23	25	11	10	10	11	11	9
123478	7	7	7	7	7	8	8	7	8	11	11	12	11	11	13
123678	7	7	6	6	6	7	6	7	6	10	11	11	11	11	12
123479	1	2	2	1	1	1	1	1	1	2	2	2	2	2	2
123469	5	5	5	2	2	2	2	3	2	2	2	2	2	2	1
123679	2	2	2	1	1	1	1	1	1	3	3	3	3	3	2
234678+	18	17	12	8	7	8	9	11	8	14	13	12	14	13	12
123789+	5	4	4	1	1	2	1	3	1	3	3	3	2	2	2
1234678	46	56	58	85	86	84	83	71	86	56	59	58	57	60	70
1234679	25	19	20	9	8	8	9	14	8	20	18	18	16	18	13
1234689	19	17	15	4	4	5	4	10	4	15	14	14	11	13	9
1234789	10	8	7	2	2	3	4	6	2	10	9	10	16	9	7