



# Atmospheric dry deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the vicinity of municipal solid waste incinerators

Yee-Lin Wu<sup>a,b</sup>, Long-Full Lin<sup>c,\*</sup>, Lien-Te Hsieh<sup>d</sup>, Lin-Chi Wang<sup>e</sup>, Guo-Ping Chang-Chien<sup>e</sup>

<sup>a</sup> Department of Environmental Engineering, National Cheng Kung University, 1 University Road, Tainan 70101, Taiwan

<sup>b</sup> Sustainable Environment Research Center, National Cheng Kung University, 1 University Road, Tainan 70101, Taiwan

<sup>c</sup> Department of Environmental Engineering, Kun Shan University, 949 Da Wan Road, Tainan 71003, Taiwan

<sup>d</sup> Department of Environmental Science and Engineering, National Pingtung University of Science and Technology, No. 1, Shuehfu Road., Pingtung 91201, Taiwan

<sup>e</sup> Department of Chemical and Materials Engineering, Cheng Shiu University, 840 Chengching Road, Kaohsiung County 833, Taiwan

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## ABSTRACT

This study focuses on the atmospheric dry deposition flux of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in the vicinity of the two municipal solid waste incinerators (MSWIs) located in southern Taiwan. PCDD/Fs in ambient air were taken and analyzed for seventeen 2,3,7,8-substituted PCDD/Fs during November 2004 and July 2005. Results show that the mean concentrations of PCDD/Fs in the ambient air near MSWI-GS and MSWI-RW were 0.090 and 0.097 pg I-TEQ/Nm<sup>3</sup>, respectively. Dry deposition fluxes of total PCDD/Fs were 18.0 and 23.5 pg I-TEQ/(m<sup>2</sup> d) in the ambient air near MSWI-GS and MSWI-RW, respectively, which were considerably higher than that measured in Guangzhou, China. Annual dry deposition fluxes of total PCDD/Fs in the ambient air near MSWI-GS and MSWI-RW were 189 and 217 ng/(m<sup>2</sup> year), respectively, which were also much higher than dry deposition of total PCDD/Fs to the Atlantic Ocean. The results of the present study strongly suggest that exposure to PCDD/Fs in this area should be reduced. In addition, parametric sensitivity shows that dry deposition flux of PCDD/Fs is most sensitive to dry deposition velocity of the particle-phase, followed by air temperature and concentration of total suspended particulate but least sensitive to dry deposition velocity of the gas-phase.

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## 1. Introduction

Owing to the adverse health effects of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), such as hormonal [1], and reproductive effects [2], their presence in the environment is of great concern.

PCDD/Fs are well-known persistent organic pollutants (POPs) that remain intact in the environment for long periods [3]. For the reference year 2000 in the United States, the total release was 1422 g TEQ/year, and release to air accounted for 92% [4]. This means that atmosphere is a major pathway for the transport of PCDD/Fs. Atmospheric deposition is a key process affecting the global sinks of POPs [5] and thus gas–particle partitioning of PCDD/Fs in the atmosphere will affect such deposition processes [6,7].

In order to get enough samples for analysis of PCDD/Fs, collectors for the determination of deposition usually stand outside for a month, thus PCDD/Fs in deposition were subjected to photolysis and then the results were lower [8]. In addition, there are certain sampling artefacts which can influence the true result of gas–particle distribution. These artefacts include blow-off from particles collected on the filter and adsorption to the filter substrate material [6]. Therefore, gas–particle partitioning and atmospheric deposition of PCDD/Fs were determined by model calculation in the present study.

In this study, atmospheric dry depositions of PCDD/Fs in the ambient air near two municipal solid waste incinerators (MSWIs) located in southern Taiwan were investigated. A total of 56 ambient air samples were taken and analyzed for 2,3,7,8-substituted PCDD/Fs from November 2004 to July 2005. Atmospheric dry deposition flux and annual dry deposition were determined by model calculations. In addition, effects of various environmental parameters on the atmospheric dry deposition fluxes of PCDD/Fs were investigated by sensitivity analysis.

\* Corresponding author. Tel.: +886 6 2050394; fax: +886 6 2052039.

E-mail address: [longfull@mail.ksu.edu.tw](mailto:longfull@mail.ksu.edu.tw) (L.-F. Lin).

**Table 1**  
Basic information for the municipal solid waste incinerators

MSWIs	GS	RW
Design type	Modular incinerator with excess-air	Modular incinerator with excess-air
Operation type	Continuous	Continuous
Feeding waste	Municipal solid waste	Municipal solid waste
Capacity	1350 tons/d	1350 tons/d
Emission temperature of stack flue gas	150 °C	135 °C
Stack height	60 m	120 m
Stack diameter	2000 mm	2140 mm
Design emission velocity of stack flue gas	16 m/s	18 m/s
Air pollution control devices in sequence	Selective non-catalytic reduction (SNCR) + semi-dry scrubber + activated carbon injection + fabric filter	Selective non-catalytic reduction (SNCR) + semi-dry scrubber + activated carbon injection + fabric filter
Average concentrations of PCDD/Fs in flue gases during sampling periods	0.025 ng I-TEQ/Nm <sup>3</sup>	0.097 ng I-TEQ/Nm <sup>3</sup>
Regulatory emission standard of PCDD/Fs	0.1 ng I-TEQ/Nm <sup>3</sup>	0.1 ng I-TEQ/Nm <sup>3</sup>

## 2. Materials and methods

### 2.1. Sampling of PCDD/Fs from the ambient air

All the samples of ambient air were collected from two MSWIs, MSWI-GS and MSWI-RW. The basic information for these two MSWIs was shown in Table 1. These two MSWIs were taken for the treatment of municipal solid wastes generated from the whole city with a population of 1.24 millions. Exposure to PCDD/Fs from the emissions of these two MSWIs was of great concern to the public.

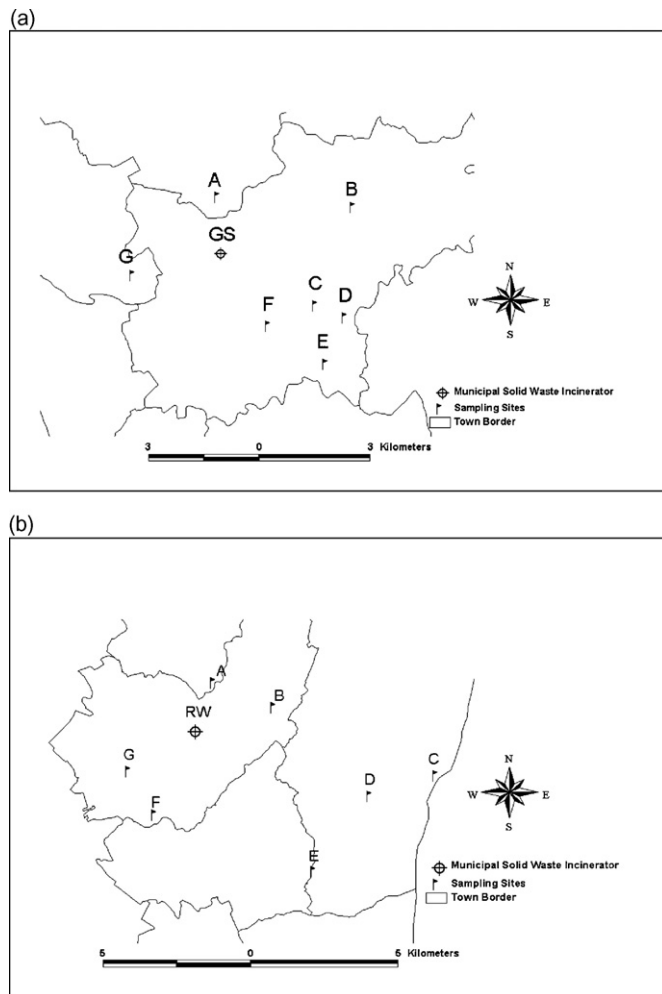
Meteorological information showed that the prevailing wind directions were northern and northwestern. The areas of maximum ground concentrations from the emissions of these two MSWIs were found by the US EPA's non-reactive Gaussian air quality dispersion model, the Industrial Source Complex Short-Term Model (ISCST-Version 3), and were selected as sampling sites. Some upwind sites were also selected. Fig. 1 shows the sampling sites. The ambient air near these two MSWIs was sampled around each in four seasons. In each sampling period, seven ambient air samples were collected simultaneously.

Each ambient air sample was collected using a polyurethane foam (PUF) sampler (Graseby Anderson, GA, USA) according to the revised US EPA Compendium Method TO-9A. The flow rate of sampler was set at 0.225 m<sup>3</sup>/min. Each sample was collected continuously on three consecutive days, yielding a sampling volume of about 972 m<sup>3</sup>. The PUF sampler was equipped with quartz-fiber filter for sampling particle-phase PCDD/Fs, and followed by a glass cartridge containing PUF for sampling gas-phase PCDD/Fs, respectively. A known amount of surrogate standard was spiked to the PUF in the laboratory prior to the field sampling was conducted. Details are similar to that given in our previous work [9].

### 2.2. Analyses of PCDD/Fs

PCDD/F analyses of ambient air followed the US EPA Compendium Method TO-9A. All chemical analyses were conducted by the Super Micro-Mass Research and Technology Center in Cheng Shiu University, certified by the Taiwan EPA for analyzing PCDD/Fs. Each collected sample was spiked with a known amount of the internal standard solution to the extraction thimble prior to PCDD/F analysis. After being extracted for 24 h, the extract was concentrated and treated with concentrated sulphuric acid, and this was followed by a series of sample cleanup and fractionation procedures. The elute was concentrated to approximately 1 mL and transferred to a vial. The concentrate was further concentrated to near dryness using a stream of nitrogen. A high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HGMS) was used for PCDD/F analyses. The HRGC (Hewlett Packard 6970

Series, CA, USA) was equipped with splitless injection and a DB-5 fused silica capillary column (60 m length, 0.25 mm i.d., and 0.25 μm film thickness) (J&W Scientific, CA, USA). The oven temperature program was set as follows: begin at 150 °C (held for 1 min), then increase at 30 °C/min to 220 °C (held for 12 min), then increase at 1.5 °C/min to 240 °C (held for 5 min), and finally increase at 1.5 °C/min to 310 °C (held for 20 min). Helium was used as the carrier gas. The HRMS (Micro-Mass Autospec Ultima, Manchester, UK) was equipped with a positive electron impact (EI+) source. The



**Fig. 1.** Sampling sites of ambient air in the vicinity of (a) MSWI-GS and (b) MSWI-RW.

selected ion monitoring analyzer mode had a resolving power of 10,000. The electron energy and source temperature were specified at 35 eV and 250 °C, respectively. Details are similar to that given in our previous works [9–11].

### 2.3. QA/QC

The Super Micro-Mass Research and Technology Center in Cheng Shiu University had participated in the sixth to ninth round of the International Intercomparison Study (from years 2001 to 2004) held by Environmental Chemistry, Department of Chemistry, Umeå University, Umeå, Sweden (the participant code of this laboratory is 57), and had a good agreement with other qualified laboratories in the world. The protocol for QA/QC was strictly followed, e.g., immediately prior to analysis, the standard solution was added to the sample to ensure recovery during the analysis process. The recovery efficiency of known-addition analysis ranged from 75 to 118%. The MDLs ranged from 0.0001 to 0.0035 ng/Nm<sup>3</sup> [11].

### 2.4. Gas-particle partitioning

The distribution of PCDD/Fs between the gas and particle-phases depends upon the particle concentration, particle size distribution, face related properties, the ambient temperature, the relative humidity and the compounds themselves [6].

An equation that has been used with success to describe gas-particle partitioning is

$$K_p = \frac{F/A}{TSP} \quad (1)$$

where  $K_p$  (m<sup>3</sup>/μg) is a temperature-dependent partitioning constant, TSP (μg/m<sup>3</sup>) is the concentration of total suspended particulate,  $F$  (pg/m<sup>3</sup>) is the concentration of the compound of interest bound to particles, and  $A$  (pg/m<sup>3</sup>) is the gaseous concentration of the compound of interest [12,13]. Plotting  $\log K_p$  against

the logarithm of the subcooled liquid vapor pressure,  $P_L^0$ , gives

$$\log K_p = m_r \log P_L^0 + b_r \quad (2)$$

where  $m_r$  is the slope and  $b_r$  is the y-intercept of the trend line.

Eitzer and Hites [14] have correlated  $P_L^0$  of PCDD/Fs with gas chromatographic retention indexes (GC-RI) on a non-polar (DB-5) GC-column using *p,p'*-DDT as a reference standard. This correlation has been redeveloped by Hung et al. [15]:

$$\log P_L^0 = \frac{-1.34 \text{ RI}}{T} + 1.67 \times 10^{-3} \text{ RI} \frac{-1320}{T} + 8.087 \quad (3)$$

where  $P_L^0$  is the subcooled liquid vapor pressure, RI is the gas chromatographic retention indexes derived by Donnelly et al. [16] and Hale et al. [17], and  $T$  is ambient temperature (K). In this study, the RIs derived by Donnelly et al. [16] and Hale et al. [17] and Eq. (3) redeveloped by Hung et al. [15] were taken to generate the  $P_L^0$  values.

Complete datasets on the gas-particle partitioning of PCDD/Fs in Taiwan have been reported [18]. Their data gave values for  $m_r = -1.29$  and  $b_r = -7.2$  with  $R^2 = 0.94$ . In this study, the trend line proposed by Chao et al. [18] was taken to estimate partitioning constant,  $K_p$ .

### 2.5. Dry deposition processes of PCDD/Fs

The dry deposition flux of PCDD/Fs was a combination of both the gas-phase and the particle-phase flux, which is given by

$$\begin{aligned} F_T &= F_g + F_p \\ C_T V_{d,T} &= C_g V_{d,g} + C_p V_{d,p} \end{aligned} \quad (4)$$

where  $F_T$  is the total PCDD/F deposition flux contributed by the summation of both the gas-phase and the particle-phase,  $F_g$  is the PCDD/F deposition flux contributed by the gas-phase,  $F_p$  is the PCDD/F deposition flux contributed by the particle-phase,  $C_T$  is the measured concentration of total PCDD/Fs in ambient air,  $V_{d,T}$  is the dry deposition velocity of total PCDD/Fs,  $C_g$  is the calculated

**Table 2**  
Concentrations of PCDD/Fs in the ambient air near MSWIS

PCDD/Fs	MSWI-GS			MSWI-RW		
	Range (n=28) (pg/Nm <sup>3</sup> )	Mean (n=28) (pg/Nm <sup>3</sup> )	R.S.D. (n=28) (%)	Range (n=28) (pg/Nm <sup>3</sup> )	Mean (n=28) (pg/Nm <sup>3</sup> )	R.S.D. (n=28) (%)
2,3,7,8-TeCDD	ND–0.013	0.005	64	ND–0.011	0.004	65
1,2,3,7,8-PeCDD	0.005–0.020	0.012	31	0.004–0.029	0.012	65
1,2,3,4,7,8-HxCDD	0.004–0.019	0.010	41	0.003–0.030	0.012	78
1,2,3,6,7,8-HxCDD	0.008–0.045	0.022	41	0.006–0.064	0.026	74
1,2,3,7,8,9-HxCDD	0.005–0.034	0.019	43	0.005–0.050	0.021	73
1,2,3,4,6,7,8-HpCDD	0.052–0.404	0.172	56	0.053–0.457	0.191	71
OCDD	0.122–1.89	0.646	68	0.118–1.46	0.538	74
2,3,7,8-TeCDF	0.022–0.103	0.056	36	0.020–0.099	0.049	50
1,2,3,7,8-PeCDF	0.023–0.104	0.053	34	0.017–0.117	0.050	60
2,3,4,7,8-PeCDF	0.030–0.112	0.073	29	0.024–0.179	0.079	63
1,2,3,4,7,8-HxCDF	0.034–0.140	0.082	36	0.020–0.232	0.092	69
1,2,3,6,7,8-HxCDF	0.027–0.121	0.072	38	0.018–0.217	0.083	75
1,2,3,7,8,9-HxCDF	0.003–0.016	0.008	53	0.002–0.058	0.011	103
2,3,4,6,7,8-HxCDF	0.031–0.116	0.071	32	0.020–0.246	0.089	78
1,2,3,4,6,7,8-HpCDF	0.082–0.343	0.224	38	0.062–0.783	0.290	72
1,2,3,4,7,8,9-HpCDF	0.015–0.064	0.037	36	0.010–0.139	0.048	73
OCDF	0.046–0.572	0.225	52	0.050–1.44	0.403	106
PCDDs	0.211–2.40	0.887	62	0.189–2.08	0.805	70
PCDFs	0.347–1.44	0.900	35	0.244–3.03	1.19	77
PCDDs/PCDFs ratio	0.457–2.12	0.95	43	0.326–1.77	0.75	41
Total PCDD/Fs	0.558–3.54	1.79	44	0.465–5.07	2.00	72
PCDDs (I-TEQ)	0.006–0.031	0.019	38	0.004–0.040	0.019	61
PCDFs (I-TEQ)	0.030–0.109	0.071	29	0.022–0.184	0.078	65
PCDDs/PCDFs I-TEQ ratio	0.156–0.371	0.26	25	0.163–0.392	0.25	23
Total PCDD/Fs (I-TEQ)	0.038–0.136	0.090	30	0.028–0.221	0.097	64

concentration of PCDD/Fs in gas-phase,  $V_{d,g}$  is the dry deposition velocity of the gas-phase PCDD/Fs,  $C_p$  is the calculated concentration of PCDD/Fs in the particle-phase, and  $V_{d,p}$  is the dry deposition velocity of the particle-phase PCDD/Fs.

Dry deposition velocities of total PCDD/Fs proposed by Shih et al. [19], which were 0.45, 0.52, 0.32, and 0.39 cm/s in spring, summer, fall, and winter, respectively, were also used here for the calculation of dry deposition flux of total PCDD/Fs.

Dry deposition of gas-phase PCDD/Fs is mainly by diffusion, and because of a lack of measured data for PCDD/Fs, a selected value (0.010 cm/s) for gas-phase polycyclic aromatic hydrocarbon (PAH) dry deposition velocity,  $V_{d,g}$ , proposed by Sheu et al. [20] and used by Lee et al. [21], is also used here to calculate the PCDD/F dry deposition flux contributed by its gas-phase.

On the other hand, dry deposition of particle-phase PCDD/Fs is mainly by gravitational settling, and the dry deposition velocity of particle-phase PCDD/Fs,  $V_{d,p}$ , can be calculated by Eq. (4).

### 3. Results and discussions

#### 3.1. Concentrations of PCDD/Fs in the ambient air near MSWIs

Table 2 lists the concentrations of PCDD/Fs in the ambient air near the two MSWIs. The concentrations of total PCDD/Fs near MSWI-GS ranged from 0.038 to 0.136 pg I-TEQ/Nm<sup>3</sup>, with an average of 0.090 pg I-TEQ/Nm<sup>3</sup> and R.S.D. of 30% ( $n = 28$ ). For MSWI-RW, the concentrations of total PCDD/Fs near MSWI-RW ranged from 0.028 to 0.221 pg I-TEQ/Nm<sup>3</sup>, with an average of 0.097 pg I-TEQ/Nm<sup>3</sup> and R.S.D. of 64% ( $n = 28$ ). These concentrations are very similar to those in residential and traffic areas, which were 0.088 and 0.073 pg I-TEQ/Nm<sup>3</sup>, respectively, but lower than those in the highly industrialized urban area also located in southern Taiwan, which was 0.15 pg I-TEQ/Nm<sup>3</sup> [22]. At present, environmental air quality standard of PCDD/Fs was not established in Taiwan, but in comparison with that regulated by the government of Japan, 0.6 pg WHO-TEQ/m<sup>3</sup>, these concentrations are still under this regulation.

Fig. 2 shows the congener profiles of seventeen 2,3,7,8-substituted PCDD/Fs measured from the ambient air near the two MSWIs. The pattern is very similar and OCDD is the dominant congener, followed by 1,2,3,4,6,7,8-HpCDF, OCDF, and 1,2,3,4,6,7,8-HpCDD. These congener profiles are also similar to those in residential and traffic areas, but different to those in the highly industrialized urban area located in southern Taiwan [22].

#### 3.2. Gas-particle partitioning

The ambient air temperature near MSWI-GS ranged from 21.6 to 29.7 °C during the four sampling periods, and the TSP ranged from 122 to 252 μg/m<sup>3</sup>. On the other hand, the ambient air temperature near MSWI-RW ranged from 17.7 to 30.3 °C during the four sampling periods, and the TSP ranged from 91 to 311 μg/m<sup>3</sup>.

Based on the environmental conditions stated above, the sub-cooled liquid vapor pressure ( $P_L^0$ ) and gas-particle partitioning constant ( $K_p$ ) for individual congener of PCDD/Fs in the ambient air can be calculated and then gas-particle partitioning can be determined. Tables 3 and 4 represent the gas-particle partitioning in the ambient air near MSWI-GS and MSWI-RW, respectively. The results show that congeners with higher chlorine number, particle-phase dominate, but the congeners with lower chlorine number, gas-phase dominate. The results also show that total PCDD/Fs is dominated by its particle-phase, but total PCDD/Fs I-TEQ is dominated by its gas-phase.

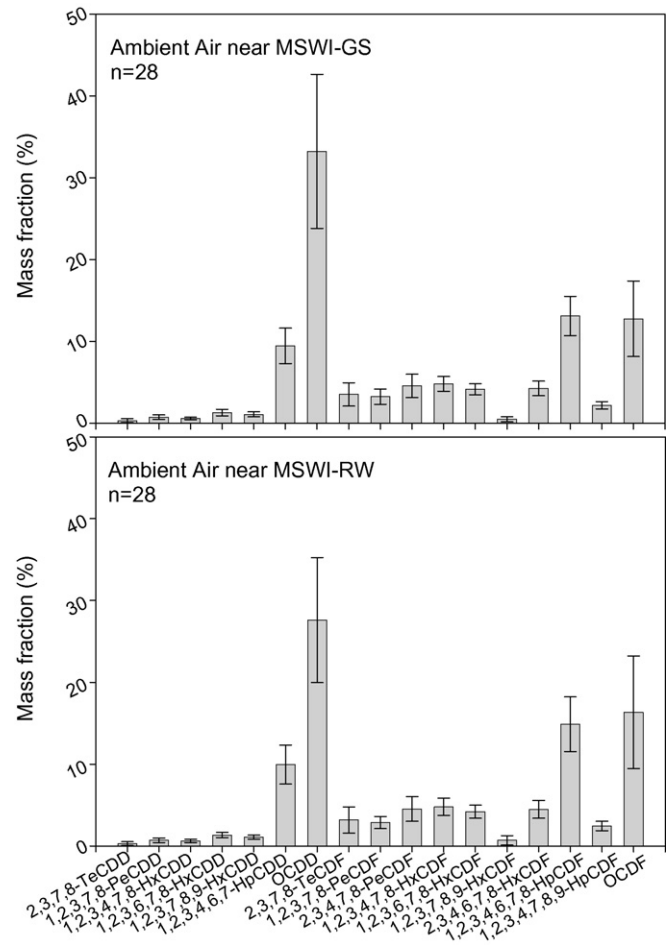


Fig. 2. Congener profiles of seventeen 2,3,7,8-substituted PCDD/Fs in the ambient air near MSWIs.

#### 3.3. Dry deposition flux of PCDD/Fs

Dry deposition flux of PCDD/Fs can be calculated by Eq. (4). In this equation, the term  $C_T$  was measured;  $C_g$  and  $C_p$  were determined according to the gas-particle partitioning shown in Tables 3 and 4;  $V_{d,T}$  and  $V_{d,g}$  were assumed; and then the unique term remains unknown,  $V_{d,p}$ , can be determined. Table 5 lists the dry deposition fluxes and dry deposition velocities of total PCDD/Fs.  $V_{d,p}$  ranged from 0.45 to 0.65 and 0.44 to 0.68 cm/s for the ambient air near MSWI-GS and MSWI-RW, respectively.

Dry deposition fluxes of individual congener is also shown in Table 6. The dry deposition fluxes of total PCDD/Fs in different seasons ranged from 5.07 to 26.1 pg I-TEQ/(m<sup>2</sup> d), with an average of 18.0 pg I-TEQ/(m<sup>2</sup> d), and ranged from 3.72 to 56.8 pg I-TEQ/(m<sup>2</sup> d), with an average of 23.5 pg I-TEQ/(m<sup>2</sup> d) in the ambient air near MSWI-GS and MSWI-RW, respectively. The results show that there are no significant differences in dry deposition fluxes of total PCDD/Fs in these two areas. This is due to the fact that these two MSWIs are not the major contributors to the PCDD/Fs in ambient air near the two MSWIs. Results of our previous work showed that these two MSWIs only contribute 2.6% to the whole city with a population of 1.24 millions [11]. Results also show that dry deposition fluxes in June and July are much lower than other periods. This is because of the precipitation in June and July for the year 2005 was much higher than that of other months, and wet deposition can significantly reduce the air concentration.

**Table 3**  
Gas–particle partitioning of PCDD/Fs in the ambient air near MSWI-GS

PCDD/Fs	Sampling periods							
	23–26 November 2004		24–27 January 2005		11–14 April 2005		29 June–2 July 2005	
	G (%) <sup>a</sup>	P (%) <sup>b</sup>	G (%) <sup>a</sup>	P (%) <sup>b</sup>	G (%) <sup>a</sup>	P (%) <sup>b</sup>	G (%) <sup>a</sup>	P (%) <sup>b</sup>
2,3,7,8-TeCDD	86	14	86	14	91	9	97	3
1,2,3,7,8-PeCDD	54	46	52	48	66	34	84	16
1,2,3,4,7,8-HxCDD	19	81	17	83	28	72	52	48
1,2,3,6,7,8-HxCDD	18	82	16	84	27	73	51	49
1,2,3,7,8,9-HxCDD	16	84	15	85	24	76	48	52
1,2,3,4,6,7,8-HpCDD	4	96	3	97	6	94	16	84
OCDD	1	99	1	99	1	99	4	96
2,3,7,8-TeCDF	90	10	90	10	94	6	98	2
1,2,3,7,8-PeCDF	70	30	68	32	79	21	91	9
2,3,4,7,8-PeCDF	62	38	60	40	74	26	88	12
1,2,3,4,7,8-HxCDF	30	70	28	72	41	59	67	33
1,2,3,6,7,8-HxCDF	29	71	27	73	40	60	66	34
1,2,3,7,8,9-HxCDF	20	80	18	82	29	71	54	46
2,3,4,6,7,8-HxCDF	23	77	21	79	34	66	59	41
1,2,3,4,6,7,8-HpCDF	8	92	7	93	13	87	30	70
1,2,3,4,7,8,9-HpCDF	4	96	3	97	6	94	17	83
OCDF	1	99	1	99	2	98	5	95
PCDDs	3	97	2	98	7	93	13	87
PCDFs	21	79	22	78	33	67	49	51
Total PCDD/Fs	14	86	10	90	21	79	34	66
PCDDs (I-TEQ)	45	55	39	61	63	37	71	29
PCDFs (I-TEQ)	50	50	47	53	63	37	80	20
Total PCDD/Fs (I-TEQ)	49	51	46	54	63	37	78	22

<sup>a</sup> G: gas-phase.<sup>b</sup> P: particle-phase.

In order to see the relative importance of individual congener of 2,3,7,8-substituted PCDD/Fs, congener profiles based on dry deposition flux are also shown in Fig. 3. It shows that dry deposition flux was most dominated by OCDD, followed by OCDF, 1,2,3,4,6,7,8-

HpCDF, and 1,2,3,4,6,7,8-HpCDD. This pattern is very similar to the congener profiles of air concentrations in this study, but different to the congener profiles of dry deposition flux in rural area [19].

**Table 4**  
Gas–particle partitioning of PCDD/Fs in the ambient air near MSWI-RW

PCDD/Fs	Sampling periods							
	15–18 November 2004		31 January–3 February 2005		18–21 April 2005		11–14 July 2005	
	G (%) <sup>a</sup>	P (%) <sup>b</sup>	G (%) <sup>a</sup>	P (%) <sup>b</sup>	G (%) <sup>a</sup>	P (%) <sup>b</sup>	G (%) <sup>a</sup>	P (%) <sup>b</sup>
2,3,7,8-TeCDD	89	11	64	36	93	7	98	2
1,2,3,7,8-PeCDD	59	41	23	77	71	29	89	11
1,2,3,4,7,8-HxCDD	22	78	5	95	33	67	62	38
1,2,3,6,7,8-HxCDD	21	79	5	95	31	69	61	39
1,2,3,7,8,9-HxCDD	19	81	4	96	29	71	58	42
1,2,3,4,6,7,8-HpCDD	4	96	1	99	8	92	22	78
OCDD	1	99	0	100	2	98	5	95
2,3,7,8-TeCDF	92	8	73	27	95	5	98	2
1,2,3,7,8-PeCDF	74	26	38	62	82	18	94	6
2,3,4,7,8-PeCDF	67	33	30	70	77	23	92	8
1,2,3,4,7,8-HxCDF	34	66	10	90	47	53	75	25
1,2,3,6,7,8-HxCDF	33	67	9	91	46	54	74	26
1,2,3,7,8,9-HxCDF	23	77	6	94	34	66	64	36
2,3,4,6,7,8-HxCDF	27	73	7	93	39	61	68	32
1,2,3,4,6,7,8-HpCDF	9	91	2	98	15	85	38	62
1,2,3,4,7,8,9-HpCDF	5	95	1	99	8	92	23	77
OCDF	1	99	0	100	2	98	8	92
PCDDs	3	97	1	99	8	92	17	83
PCDFs	19	81	8	92	33	67	53	47
Total PCDD/Fs	12	88	5	95	24	76	38	62
PCDDs (I-TEQ)	43	57	19	81	64	36	74	26
PCDFs (I-TEQ)	52	48	23	77	66	34	84	16
Total PCDD/Fs (I-TEQ)	50	50	22	78	66	34	82	18

<sup>a</sup> G: gas-phase.<sup>b</sup> P: particle-phase.



**Table 5**  
Measured concentrations and calculated dry deposition fluxes and dry deposition velocities of total PCDD/Fs

MSWIs	Sampling periods	Dry deposition flux of total PCDD/Fs			Concentrations of total PCDD/Fs ( $n=7$ )			Dry deposition velocity of total PCDD/Fs		
		$F_{d,T}$ (pg/(m <sup>2</sup> d))	$F_{d,g}$ (pg/(m <sup>2</sup> d))	$F_{d,p}$ (pg/(m <sup>2</sup> d))	$C_T$ (pg/m <sup>3</sup> )	$C_g$ (pg/m <sup>3</sup> )	$C_p$ (pg/m <sup>3</sup> )	$V_{d,T}$ (cm/s)	$V_{d,g}$ (cm/s)	$V_{d,p}$ (cm/s)
GS	23–26 November 2004	685	2.5	683	2.034	0.284	1.750	0.39	0.01	0.45
GS	24–27 January 2005	1072	2.5	1070	2.758	0.286	2.472	0.45	0.01	0.50
GS	11–14 April 2005	707	2.8	704	1.573	0.326	1.247	0.52	0.01	0.65
GS	29 June–2 July 2005	216	2.3	214	0.782	0.265	0.516	0.32	0.01	0.48
RW	15–18 November 2004	596	1.8	594	1.767	0.211	1.556	0.39	0.01	0.44
RW	31 January–3 February 2005	1552	1.8	1551	3.993	0.211	3.782	0.45	0.01	0.47
RW	18–21 April 2005	694	3.2	691	1.545	0.365	1.180	0.52	0.01	0.68
RW	11–14 July 2005	190	2.2	188	0.688	0.260	0.428	0.32	0.01	0.51

The dry deposition fluxes obtained in this study is considerably higher than that measured in Guangzhou, China, which is only 6.2 pg WHO-TEQ/(m<sup>2</sup> d) [8]. A reasonable explanation is that the area for comparison located in a commercial district in an urban area, no large municipal solid waste incinerators, industrial waste incinerators and medical waste incinerators existed in Guangzhou. While in this study, it was located in a highly industrialized area. There are two large scale municipal solid waste incinerators (both are 1350 tons/d), a large scale power plant with 2100 MW coal-fired and 2230 MW LNG-fired capacity plus other industrial emissions existed in this area.

In order to have a better insight into dry deposition, dry deposition velocities of individual congeners were also shown in Fig. 4. The results indicate that higher chlorinated congeners have a greater dry deposition velocity. Dry deposition velocities of PCDDs, PCDFs, and total PCDD/Fs were also listed in Table 7. Dry deposition

velocities of total PCDD/Fs (I-TEQ) were 0.22 and 0.39 cm/s for the ambient air near MSWI-GS and MSWI-RW, respectively. The dry deposition velocity of total PCDD/Fs, 0.42 cm/s, was similar to that of total PAHs, which were 0.18 and 0.23 cm/s for the urban and petrochemical-industry (PCI) site, respectively [20]. This value, 0.42 cm/s, was also similar to that of total polychlorinated biphenyls (PCBs) in urban site, 0.39 cm/s, but lower than those in petroleum refinery (PR) and rural site, which were 0.88 and 0.68 cm/s, respectively [21].

#### 3.4. Annual dry deposition flux of PCDD/Fs

In order to estimate annual dry deposition flux of PCDD/Fs, the information on the number of days with precipitation in 2005 was gathered from the nearest weather station, Kaohsiung weather station.

**Table 6**  
Dry deposition fluxes of PCDD/Fs in the ambient air near MSWIs

PCDD/Fs	MSWI-GS ( $F_{d,T}$ (pg/(m <sup>2</sup> d)))				MSWI-RW ( $F_{d,T}$ (pg/(m <sup>2</sup> d)))			
	23–26 November 2004	24–27 January 2005	11–14 April 2005	29 June–2 July 2005	15–18 November 2004	31 January–3 February 2005	18–21 April 2005	11–14 July 2005
2,3,7,8-TeCDD	0.245	0.344	0.595	0.050	0.126	0.698	0.397	0.038
1,2,3,7,8-PeCDD	1.85	3.35	2.64	0.605	1.23	6.91	2.25	0.344
1,2,3,4,7,8-HxCDD	2.56	5.55	4.23	1.15	2.12	10.1	4.29	0.855
1,2,3,6,7,8-HxCDD	6.71	10.6	10.7	2.46	5.47	21.1	8.61	1.94
1,2,3,7,8,9-HxCDD	5.38	10.5	8.75	2.12	4.51	17.0	7.14	1.65
1,2,3,4,6,7,8-HpCDD	58.0	129	79.8	26.7	52.8	158	76.4	29.0
OCDD	240	536	277	86.0	227	405	218	73.3
2,3,7,8-TeCDF	2.63	3.02	2.85	0.648	1.25	8.50	2.48	0.400
1,2,3,7,8-PeCDF	8.65	8.64	6.42	1.35	4.18	23.5	5.09	0.829
2,3,4,7,8-PeCDF	12.6	14.4	12.7	2.53	6.51	40.6	12.0	1.67
1,2,3,4,7,8-HxCDF	28.1	34.8	23.3	6.36	19.1	64.7	24.9	4.30
1,2,3,6,7,8-HxCDF	25.4	30.9	21.6	5.19	15.3	64.2	22.1	3.64
1,2,3,7,8,9-HxCDF	1.72	2.35	5.46	0.879	1.36	4.47	9.58	0.692
2,3,4,6,7,8-HxCDF	23.0	33.2	26.0	7.20	15.8	72.9	25.2	5.33
1,2,3,4,6,7,8-HpCDF	109	118	92.2	33.4	89.4	217	123	30.3
1,2,3,4,7,8,9-HpCDF	18.3	19.3	18.3	6.56	15.9	35.2	23.1	5.66
OCDF	139	110	111	33.3	131	387	132	31.0
PCDDs	315	695	384	119	294	619	317	107
PCDFs	368	375	319	97.4	300	919	379	83.8
PCDDs/PCDFs ratio	0.966	2.03	1.38	1.44	1.13	0.77	0.99	1.54
Total PCDD/Fs	683	1070	703	216	593	1538	696	191
PCDDs (I-TEQ)	3.45	6.51	5.36	1.28	2.71	11.0	4.51	1.02
PCDFs (I-TEQ)	16.2	19.6	15.8	3.79	9.92	45.9	16.3	2.70
PCDDs/PCDFs I-TEQ ratio	0.38	0.57	0.67	0.6	0.47	0.42	0.53	0.6
Total PCDD/Fs (I-TEQ)	19.7	26.1	21.2	5.07	12.6	56.8	20.8	3.72

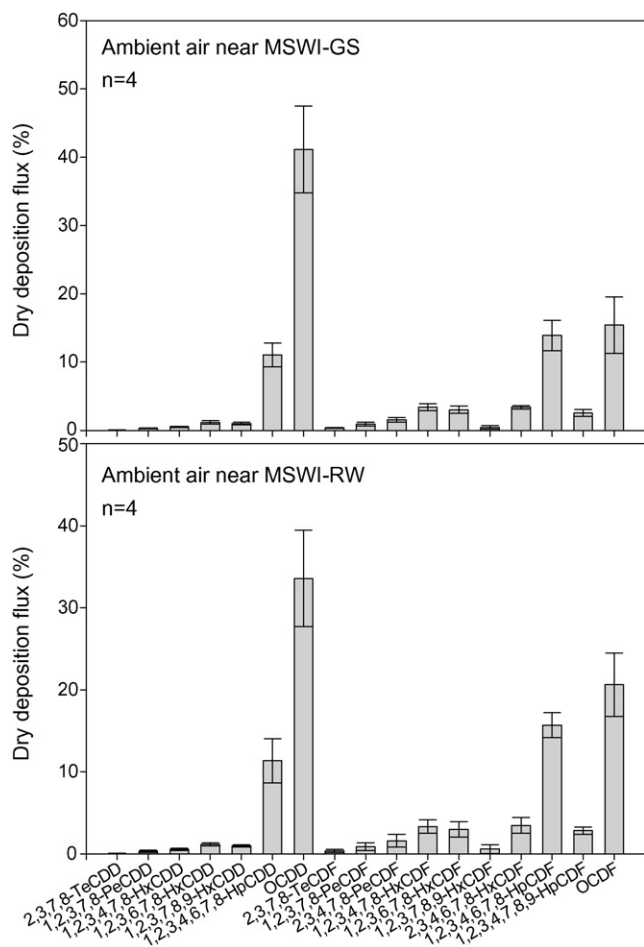


Fig. 3. Congener profiles of seventeen 2,3,7,8-substituted PCDD/F dry deposition fluxes.

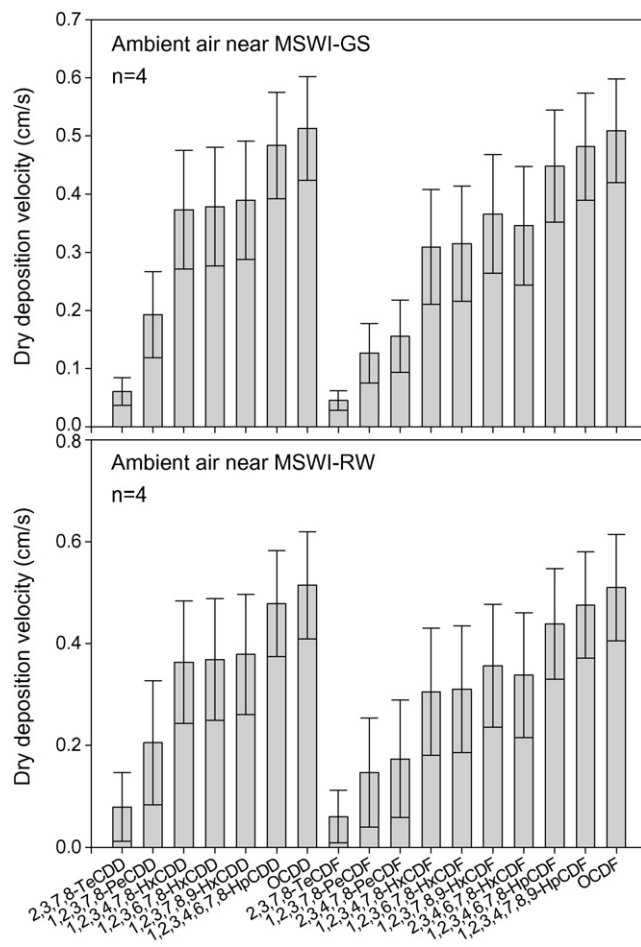


Fig. 4. Dry deposition velocity of 17 individual congeners of PCDD/Fs in the ambient air near MSWIs.

Table 8 shows the annual dry deposition flux of PCDD/Fs in the ambient air near the two MSWIs. The dry deposition fluxes of total PCDD/Fs were 189 and 217 ng/(m<sup>2</sup> year) in the ambient air near MSWI-GS and MSWI-RW, respectively. In comparison with the average dry deposition flux of total PCDD/Fs to the Atlantic Ocean, which is only 9 ng/(m<sup>2</sup> year) [5], it is suggested that exposure to PCDD/Fs in this area should be reduced.

### 3.5. Sensitivity analysis

The aim of sensitivity analysis was to gain a better insight into the relative importance of the various environmental param-

eters for the atmospheric dry deposition fluxes. All the parameters that have an effect on gas–particle partitioning and dry deposition velocity will be the influential parameters on the dry deposition flux. In this study, sensitivity of dry deposition flux to changes in the environmental parameters is focused on  $V_{d,p}$ ,  $V_{d,g}$ , TSP, and air temperature. Sensitivity analyses were performed using the initial values of  $V_{d,p} = 0.5$  cm/s,  $V_{d,g} = 0.01$  cm/s, TSP = 150  $\mu\text{g}/\text{m}^3$ , and ambient air temperature = 25 °C. All simulation was performed under a constant concentration of PCDD/Fs at 2.08  $\text{pg}/\text{Nm}^3$ . In Fig. 5, it is important to note the definition of  $P$ ,  $\Delta P$ ,  $S$ , and  $\Delta S$ :

Table 7  
Dry deposition velocities of PCDD/Fs in the ambient air near MSWIs

PCDD/Fs	MSWI-GS			MSWI-RW		
	Range (n = 4) (cm/s)	Mean (n = 4) (cm/s)	R.S.D. (n = 4) (%)	Range (n = 4) (cm/s)	Mean (n = 4) (cm/s)	R.S.D. (n = 4) (%)
PCDDs	0.42–0.61	0.49	17.5	0.42–0.63	0.49	19.7
PCDFs	0.25–0.44	0.36	22.5	0.24–0.46	0.37	25.7
PCDDs/PCDFs ratio	1.23–1.68	1.39	15.2	1.07–1.74	1.34	21.7
Total PCDD/Fs	0.32–0.52	0.42	20.1	0.32–0.52	0.42	20.3
PCDDs (I-TEQ)	0.15–0.31	0.24	28.2	0.14–0.38	0.26	39.0
PCDFs (I-TEQ)	0.11–0.27	0.21	34.2	0.09–0.36	0.23	49.3
PCDDs/PCDFs I-TEQ ratio	1.01–1.39	1.17	–	0.51–0.83	0.65	–
Total PCDD/Fs (I-TEQ)	0.11–0.28	0.22	32.9	0.11–0.72	0.39	64.7

**Table 8**  
Annual dry deposition fluxes of PCDD/Fs in the ambient air near MSWIs

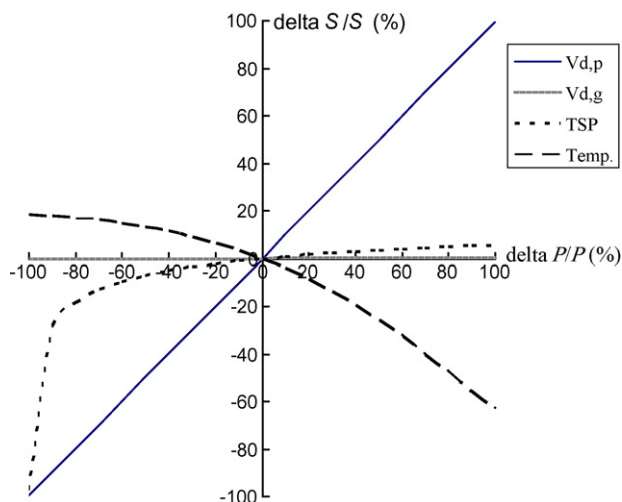
PCDD/Fs	MSWI-GS		MSWI-RW	
	$F_d$ (ng/(m <sup>2</sup> year))	% <sup>a</sup>	$F_d$ (ng/(m <sup>2</sup> year))	% <sup>a</sup>
2,3,7,8-TeCDD	0.081	86.7	0.089	91.2
1,2,3,7,8-PeCDD	0.588	97.1	0.789	98.3
1,2,3,4,7,8-HxCDD	0.936	99.4	1.250	99.6
1,2,3,6,7,8-HxCDD	2.09	99.4	2.68	99.6
1,2,3,7,8,9-HxCDD	1.85	99.5	2.19	99.6
1,2,3,4,6,7,8-HpCDD	20.6	99.9	22.5	99.9
OCDD	81.4	100.0	65.9	100.0
2,3,7,8-TeCDF	0.636	81.2	0.934	89.4
1,2,3,7,8-PeCDF	1.78	94.8	2.53	97.1
2,3,4,7,8-PeCDF	2.96	96.0	4.49	97.8
1,2,3,4,7,8-HxCDF	6.57	98.9	8.24	99.3
1,2,3,6,7,8-HxCDF	5.90	99.0	7.72	99.4
1,2,3,7,8,9-HxCDF	0.666	99.3	1.020	99.4
2,3,4,6,7,8-HxCDF	6.25	99.2	8.71	99.5
1,2,3,4,6,7,8-HpCDF	24.7	99.8	32.7	99.8
1,2,3,4,7,8,9-HpCDF	4.32	99.9	5.62	99.9
OCDF	27.4	100.0	50.0	100.0
PCDDs	108	99.9	95	99.9
PCDFs	81.2	99.3	121.9	99.6
PCDDs/PCDFs ratio	1.32	–	0.78	–
Total PCDD/Fs	189	99.6	217	99.7
PCDDs (I-TEQ)	1.15	98.1	1.39	98.8
PCDFs (I-TEQ)	3.89	97.6	5.47	98.5
PCDDs/PCDFs I-TEQ ratio	0.30	–	0.25	–
Total PCDD/Fs (I-TEQ)	5.04	97.7	6.86	98.6

<sup>a</sup> %P: annual dry deposition fluxes contributed by particle-phase deposition.

- $P$  ≡ initial value of parameters;
- $\Delta P$  ≡ increase or reduction in parameters;
- $S$  ≡ predicted value in each of the parameters at initial value;
- $\Delta S$  ≡ response in each of the parameters.

As shown in Fig. 5, dry deposition flux was most sensitive to the parameters  $V_{d,p}$ . When  $\Delta P/P$  was changed from  $-50$  to  $50\%$ ,  $\Delta S/S$  responded from  $-49.8$  to  $49.8\%$ .

The sensitivity analysis indicates that an increase in air temperature has a significant effect on dry deposition flux. When  $\Delta P/P$  was changed from  $0$  to  $50\%$ ,  $\Delta S/S$  responded from  $0$  to  $-26\%$ . But a decrease in air temperature has a less effect on dry deposition flux than an increase in air temperature. When  $\Delta P/P$  was changed from  $0$  to  $-50\%$ ,  $\Delta S/S$  responded from  $0$  to  $13\%$ .



**Fig. 5.** Parametric sensitivity for the dry deposition flux.

The sensitivity analysis also indicates that an increase in TSP has less effect than that of air temperature on dry deposition flux. When  $\Delta P/P$  was changed from  $0$  to  $50\%$ ,  $\Delta S/S$  responded from  $0$  to  $3.4\%$ . But a decrease in TSP has a more significant effect on dry deposition flux than an increase in TSP. When  $\Delta P/P$  was changed from  $0$  to  $-50$ ,  $-70$ , and  $-90\%$ ,  $\Delta S/S$  responded from  $0$  to  $-7.0$ ,  $-13$ , and  $-28\%$ , respectively.

$V_{d,g}$  is the least sensitive parameter. For a change in  $V_{d,g}$  when  $\Delta P/P$  was changed from  $-50$  to  $50\%$ ,  $\Delta S/S$  responded from  $-0.2$  to  $0.2\%$  only.

#### 4. Conclusions

The concentrations of PCDD/Fs in the ambient air near the two MSWIs were very similar to those in residential and traffic areas, but lower than those in the highly industrialized urban area located in southern Taiwan.

Calculated dry deposition fluxes of total PCDD/Fs were considerably higher than those measured in Guangzhou, China. In addition, calculated annual dry deposition fluxes of total PCDD/Fs in ambient air near the two MSWIs were also much higher than those to the Atlantic Ocean. The results of the present study strongly suggest that exposure to PCDD/Fs in this area should be reduced.

On the other hand, parametric sensitivity shows that dry deposition flux of PCDD/Fs is most sensitive to  $V_{d,p}$ , followed by air temperature and TSP, but least sensitive to  $V_{d,g}$ .

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