Supporting Information for

PAMS-Constrained Top-Down Calibration of VOC-Speciated CMAQ Simulations

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Figures S1 to S5

Tables S1 to S2

Additional text

It is noted that, in the model, the VOC speciation is based on the U.S. Source Classification Code (SCC) profiling (SPECIATE 4.5 database issued by the U.S. EPA), which is not necessarily applicable to other regions such as Taiwan. Even this database in the U.S. also needs to be constantly updated (Ying and Li, 2011). For instance, Chen et al. (Chen et al., 2010) pointed out the difference in household VOC profiling between the U.S. and Taiwan. The household fuel used in the U.S. is mainly methane in natural gas, but in addition to natural gas used in major metropolises, it is mostly LPG, composed of *propane* and *butane*, used in wider areas of Taiwan. The VOC profiles assigned for households in Taiwan are **External Combustion Boiler – Natural Gas** (0003) and **Residential Fuel – Natural Gas** (0195). While the 0195 profile is 100% methane, the 0003 profile has 56% methane and only 4% propane (**Fig. S5**). As a result, the 0003 profile is not suitable for households in Taiwan (propane should be given a higher emission factor than methane).

Other major sources could encounter similar profiling errors. Another deficiency is the lack of profiles. For instance, the default profile (Overall Average, 0000) is commonly assigned to sources without corresponding SCC profiles. Taking the top 10 emission entries with high ozone formation potentials (OFP) in a major metropolis of Taiwan (Taoyuan City with a population of 2 million) as an example, the inventory registers seven facility types, consisting of Textile Finishing (1140), Printing Service (1602), Plastic Products (2209), Integrated Circuits (2611), Other General-purpose Machinery (2939), Motor Vehicle Manufacture (3010), and Other Manufacturing Not Elsewhere Classified (3399). However, these seven industry types have no corresponding SCC profiles and thus are all being assigned as the default profile. This issue is not unique to Taiwan but is common in the U.S too. The U.S. EPA may have continued to update the database by replacing the default profile with more appropriate source profiles. For instance, in SPECIATE 4.5, 80% of the Pulp and Paper facility type is reassigned from profiles No. 0000 and 1185 to 63 separated profiles, and 22% of the Chemical Manufacturing facility type is reassigned from profile No. 0000 to 15 separated profiles (Strum et al., 2017). In other words, every time the emission inventory gets updated, the assignment of VOC profiles should also be re-examined and revised accordingly to perform more accurate OFP estimates.

It should be noted that unrealistic VOC profiling in the inventory may not be critical if ozone simulation is the aim. However, it can be error-prone if the sources with high ozone formation potentials (OFPs) of individual species are to be sought. Establishing localized speciation profiles for VOCs from key emission sources is crucial for accurately calculating OFPs and informing realistic ozone control policymaking through modeling. This approach enables the identification of key VOC species or specific sources, as outlined in the Selective Precursor Mitigation (SPM) concept (Chen et al., 2024).

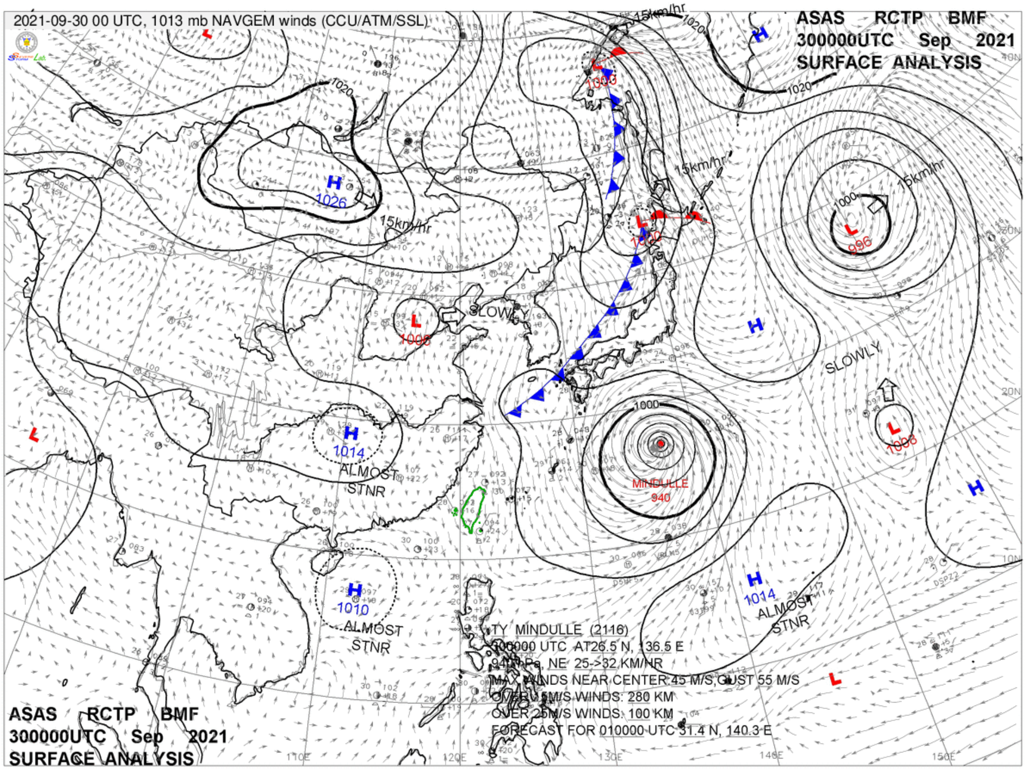


Fig. S1. Synoptic weather patterns in East Asia for the selected case in 2021.

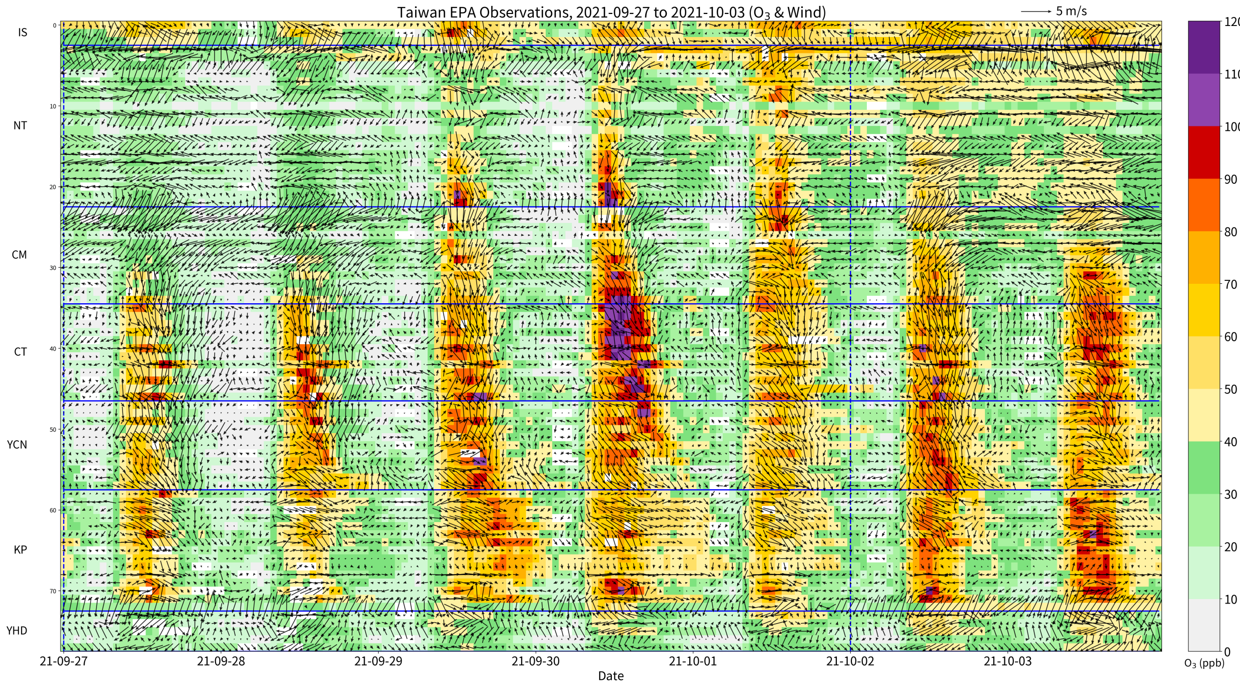
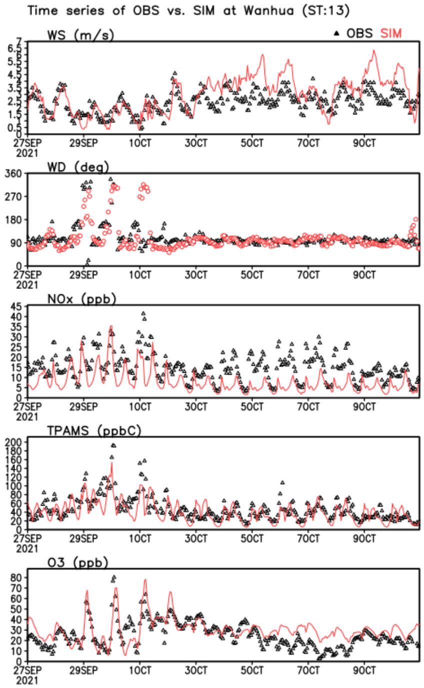
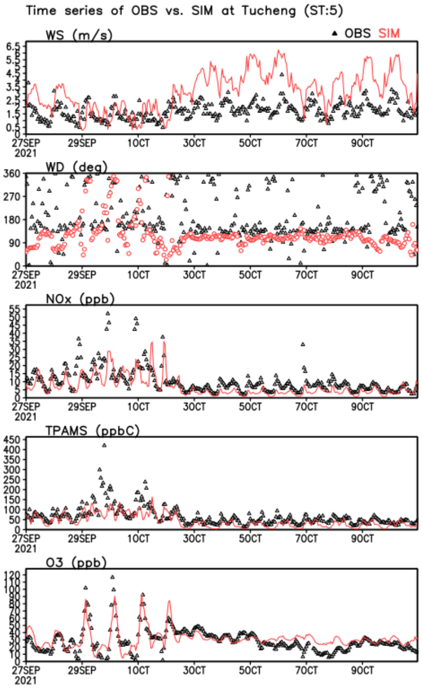
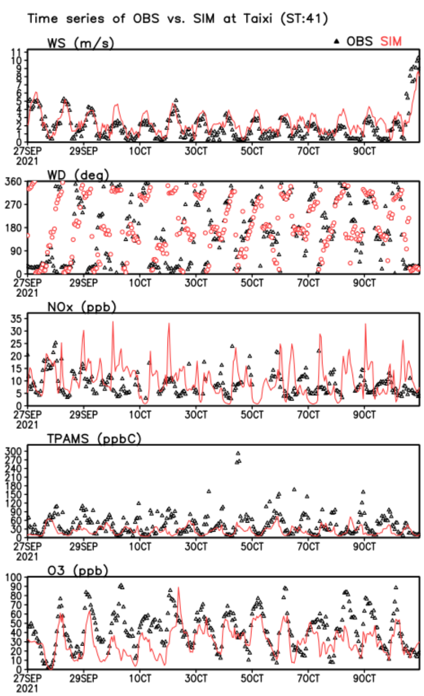
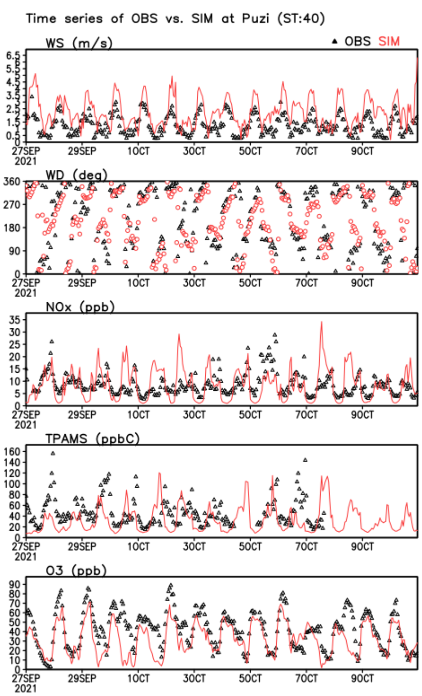


Fig. S2. Hourly observations of O_3 along with wind fields at all AQS from north to south of Taiwan (IS→NT→CM→CT→YCN→KP→YHD) for the selected case in 2021 (2021/09/27-10/10).


Time series of OBS vs. SIM at Wanhua (ST:13)
WS (m/s)
OBS SIM
WD (deg)
NOx (ppb)
TPAMS (ppbC)
O3 (ppb)
27SEP 2021
29SEP
1OCT
3OCT
5OCT
7OCT
9OCT


Time series of OBS vs. SIM at Tucheng (ST:5)
WS (m/s)
OBS SIM
WD (deg)
NOx (ppb)
TPAMS (ppbC)
O3 (ppb)
27SEP 2021
29SEP
1OCT
3OCT
5OCT
7OCT
9OCT


Time series of OBS vs. SIM at Taixi (ST:41)
WS (m/s)
OBS SIM
WD (deg)
NOx (ppb)
TPAMS (ppbC)
O3 (ppb)
27SEP 2021
29SEP
1OCT
3OCT
5OCT
7OCT
9OCT


Time series of OBS vs. SIM at Puzi (ST:40)
WS (m/s)
OBS SIM
WD (deg)
NOx (ppb)
TPAMS (ppbC)
O3 (ppb)
27SEP 2021
29SEP
1OCT
3OCT
5OCT
7OCT
9OCT

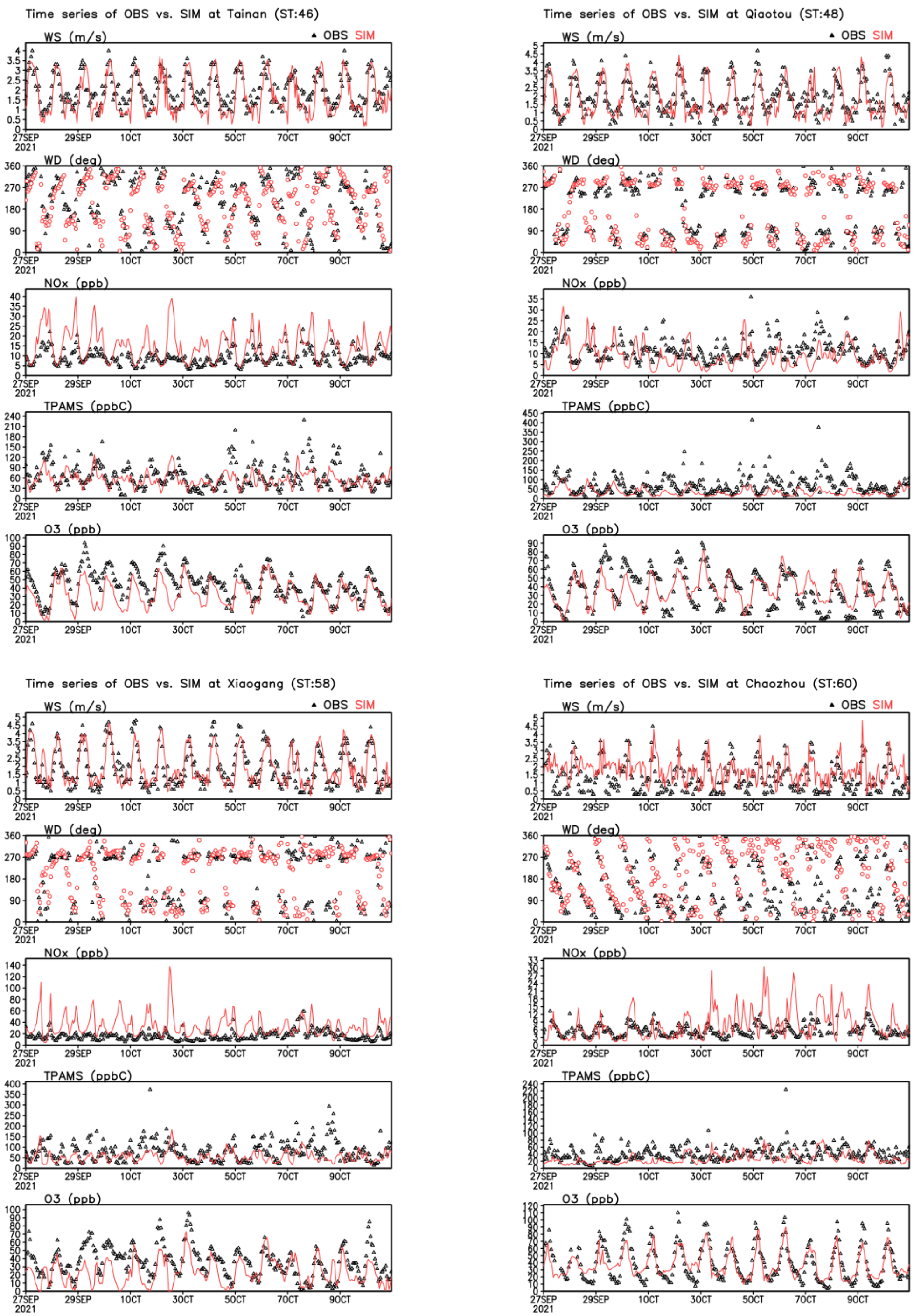
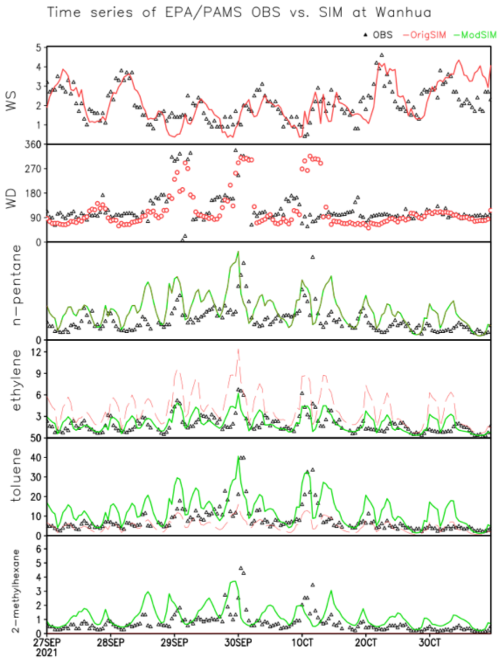
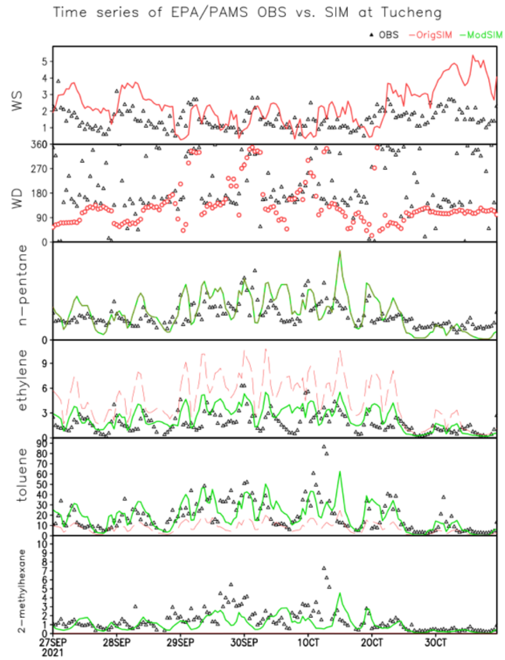


Fig. S3. Time series of observed and modeled wind fields and critical pollutants at PAMS stations for the 2021 case study.


Time series of EPA/PAMS OBS vs. SIM at Wanhua
OBS
OrigSIM
ModSIM
WS
WD
n-pentane
ethylene
toluene
2-methylhexane
27SEP
2021
28SEP
29SEP
30SEP
1OCT
2OCT
3OCT


Time series of EPA/PAMS OBS vs. SIM at Tucheng
OBS
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27SEP
2021
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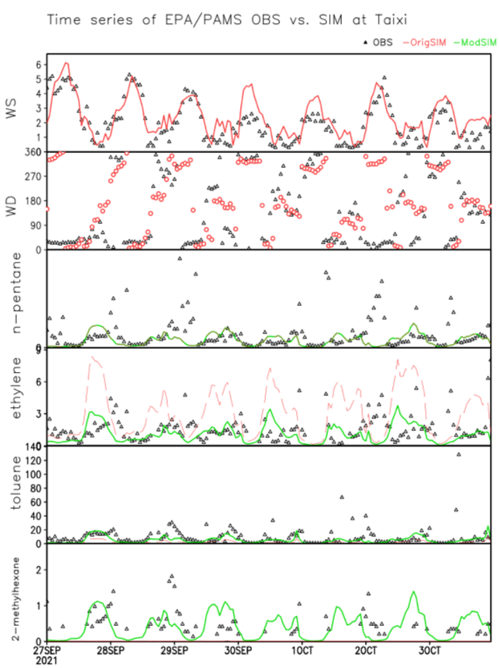
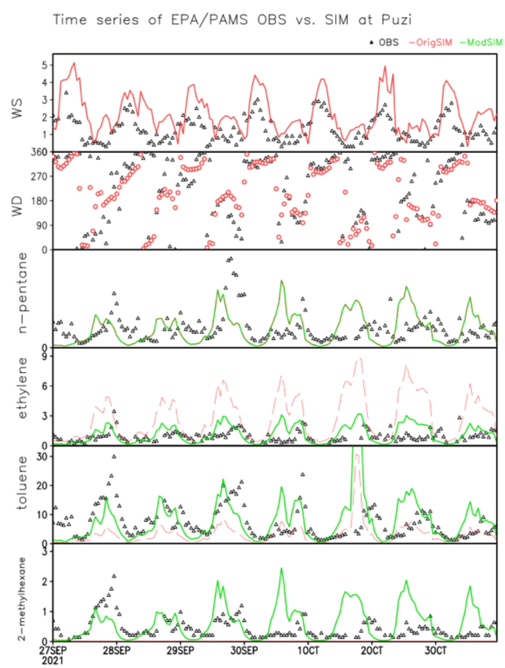
30SEP
1OCT
2OCT
3OCT


Time series of EPA/PAMS OBS vs. SIM at Taixi
OBS
OrigSIM
ModSIM
WS
WD
n-pentane
ethylene
toluene
2-methylhexane
27SEP
2021
28SEP
29SEP
30SEP
1OCT
2OCT
3OCT


Time series of EPA/PAMS OBS vs. SIM at Puzi
OBS
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29SEP
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1OCT
2OCT
3OCT

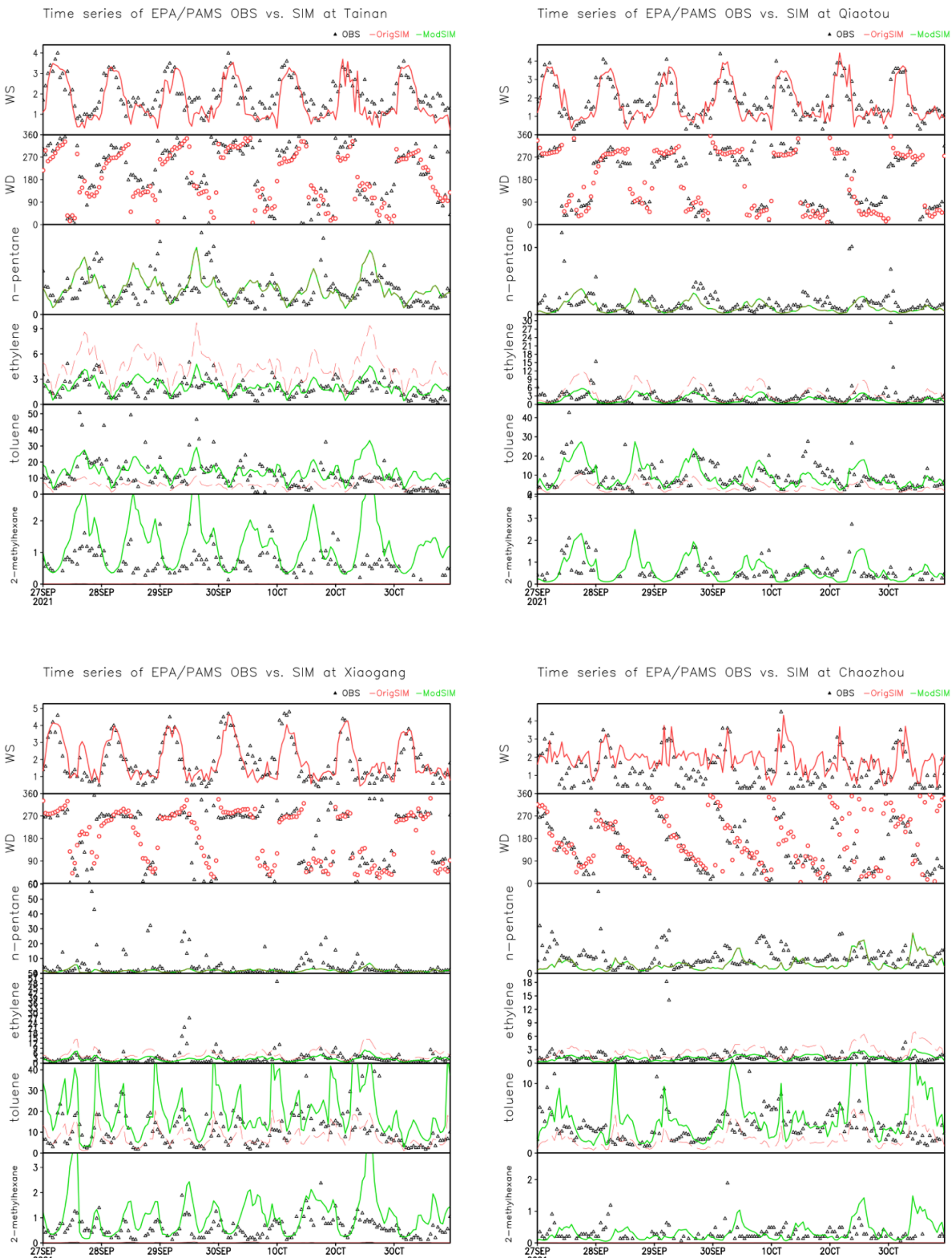

Fig. S4. All other PAMS sites exhibited similar results for PAMS species simulations (TPAMS, similar, underestimated, overestimated patterns, and zero emissions).

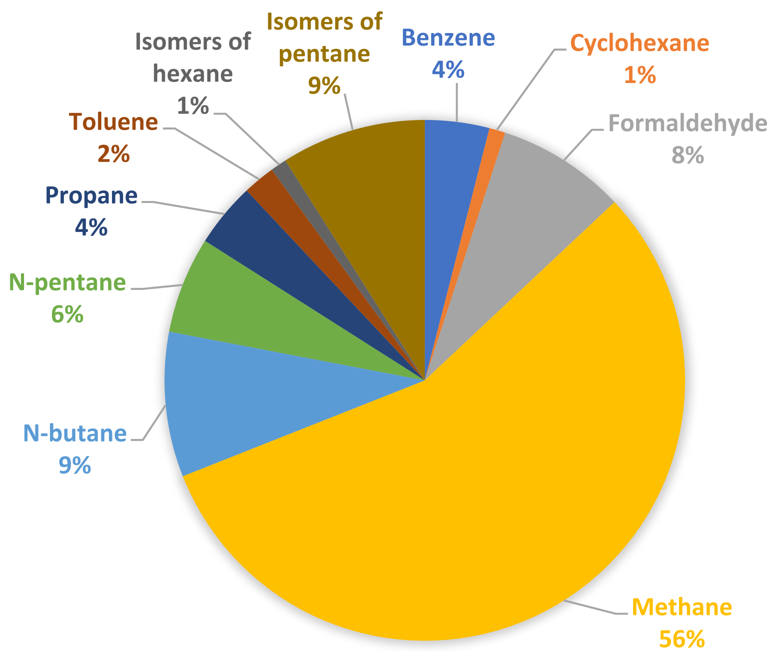

Fig. S5. VOC speciation profile for External Combustion Boiler – Natural Gas (0003).

Table S1. Comparison of model simulations with observations at all general TAQMN sites in Taiwan*.

	WS	NO_x	VOCs	O_3
Mean observed value	1.86	11.85	99.96	38.65
Mean modeled value	2.29	10.93	151.94	32.69
MB	0.43	-0.84	53.41	-5.86
RMSE	1.33	12.36	122.12	16.52
R	0.62	0.33	0.33	0.70

	WD
Mean observed value	164.16
Mean modeled value	165.35
WNMB	-0.76
WNME	13.24

*Model period is from September 27, 2021 to October 3, 2021. Definitions of model evaluation metrics can be referred to as in Chen et al. (2021).

Table S2. Averages of PAMS VOC observations and simulations.

Group	Species	ModSIM	OBS	Group	Species	ModSIM	OBS
Alkanes	propane	4.33	4.51	Alkenes	trans-2-butene	0.38	0.42
	isobutane	2.98	2.83		cis-2-butene	0.25	0.29
	n-butane	3.91	3.95		trans-2-pentene	0.27	0.29
	2,2-dimethylbutane	0.27	0.2		cis-2-pentene	0.13	0.17
	isopentane	4.15	4.08		propylene	1.07	1.4
	n-pentane	1.4	1.74		1-butene	0.45	0.55
	2,3-dimethylbutane	0.37	0.33		1-pentene	0.15	0.22
	2-methylpentane	1.06	0.86		isoprene	2.56	1.54
	3-methylpentane	0.91	0.81		ethylene	2.06	1.95
	n-hexane	1.5	1.4	Alkynes	acetylene	2.24	2.22
	2,2,4-trimethylpentane	0.73	0.97	Aromatics	benzene	0.34	1.67
	2,4-dimethylpentane	0.47	0.39		toluene	12.73	11.43
	2-methylhexane	0.94	0.8		ethylbenzene	1.4	1.31
	2,3-dimethylpentane	0.57	0.46		styrene	0.46	0.6
	3-methylhexane	0.37	0.89		isopropylbenzene	0.21	0.27
	n-heptane	0.86	0.66		n-propylbenzene	0.39	0.36
	2,3,4-trimethylpentane	0.03	0.41		m,p-xylenes	4.34	3.75
	2-methylheptane	0.29	0.24		o-xylene	1.67	1.47
	3-methylheptane	0.39	0.24		m-ethyltoluene	1	0.88
	n-octane	0.35	0.36		p-ethyltoluene	0.81	0.59
	n-nonane	0.33	0.38		o-ethyltoluene	0.71	0.44
	n-decane	0.31	0.45		1,2,4-trimethylbenzene	1.75	1.53
	n-undecane	0.32	0.36		1,2,3-trimethylbenzene	0.73	0.69
	ethane	4.24	3.93		1,3,5-trimethylbenzene	0.53	0.48
Cycloalkanes	cyclopentane	0.55	0.54		m-diethylbenzene	0.18	0.19
	methylcyclopentane	0.47	0.41		p-diethylbenzene	0.35	0.38
	cyclohexane	0.56	0.64				
	methycyclohexane	0.95	0.97				

The unit of OBS and SIM averages is ppbC.

References for SI

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