Contribution of VOCs to the SOA formation potentials from a petroleum refinery in Pearl River Delta, China

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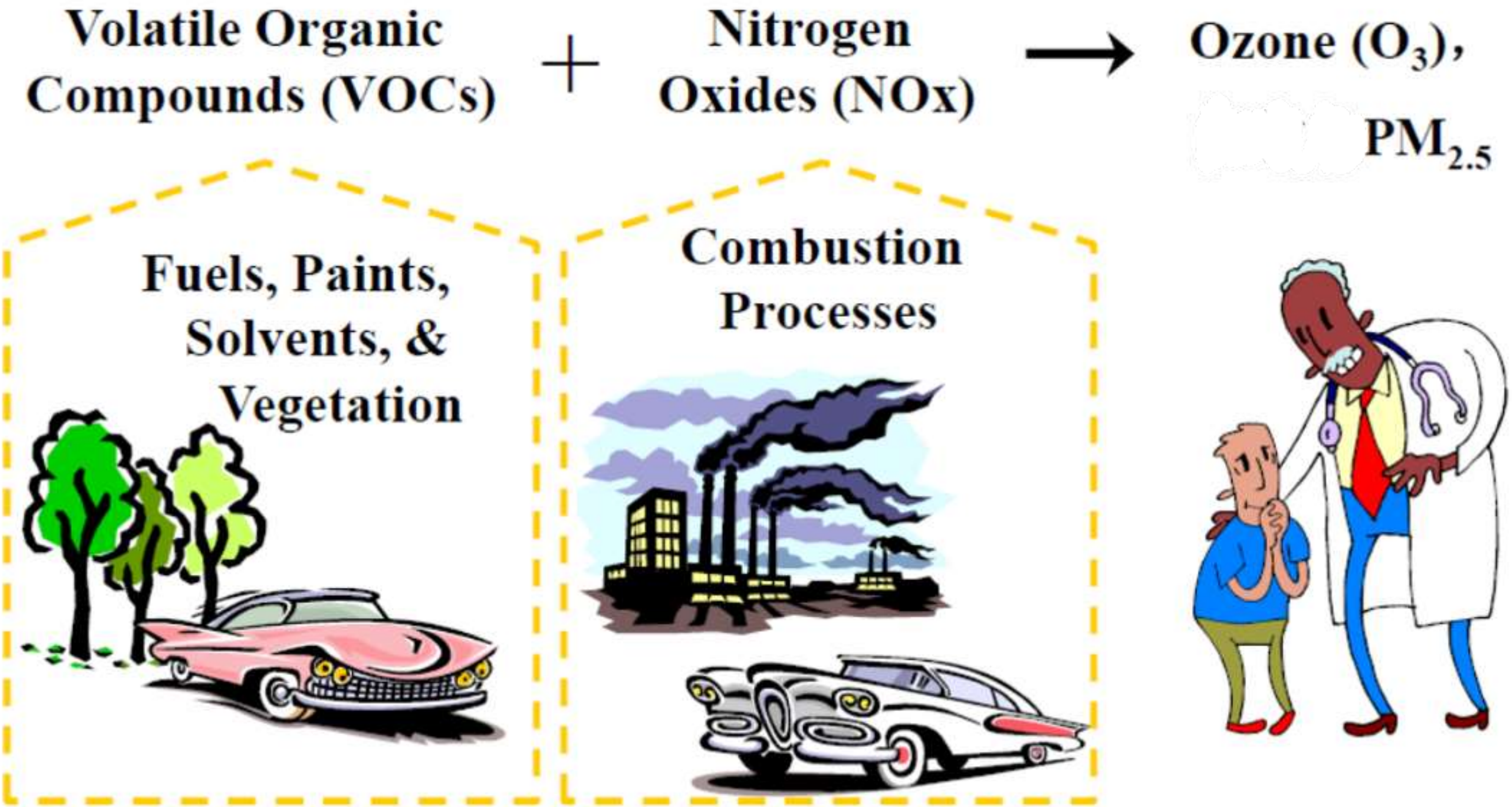
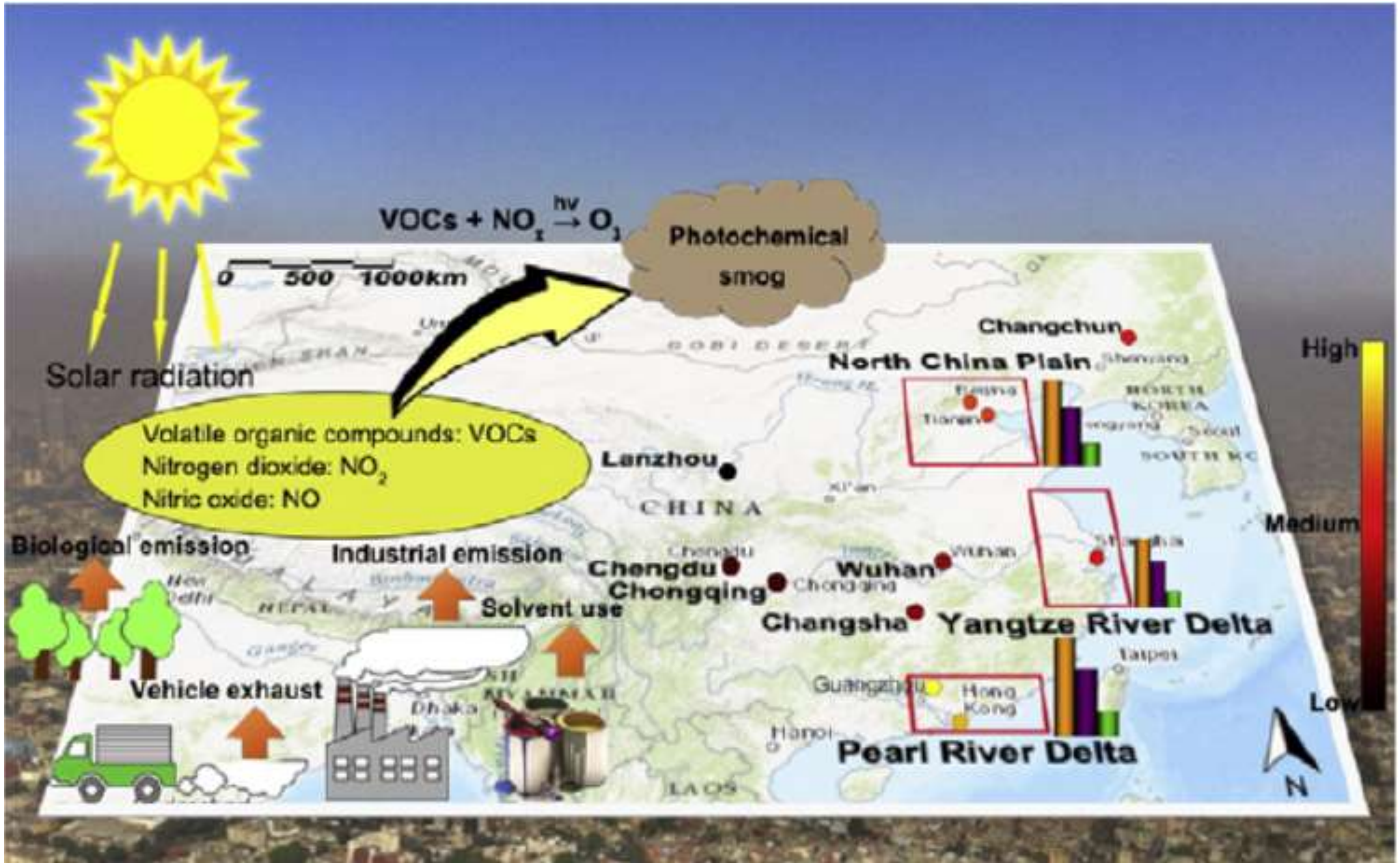
4. Summary

1. Introduction



Relationship of VOCs with O_3 and SOA



- Characteristics and sources of VOCs in China
- Relationship of VOCs with O_3 and SOA in China

Guo et al. 2017. Sci. Total Environ.

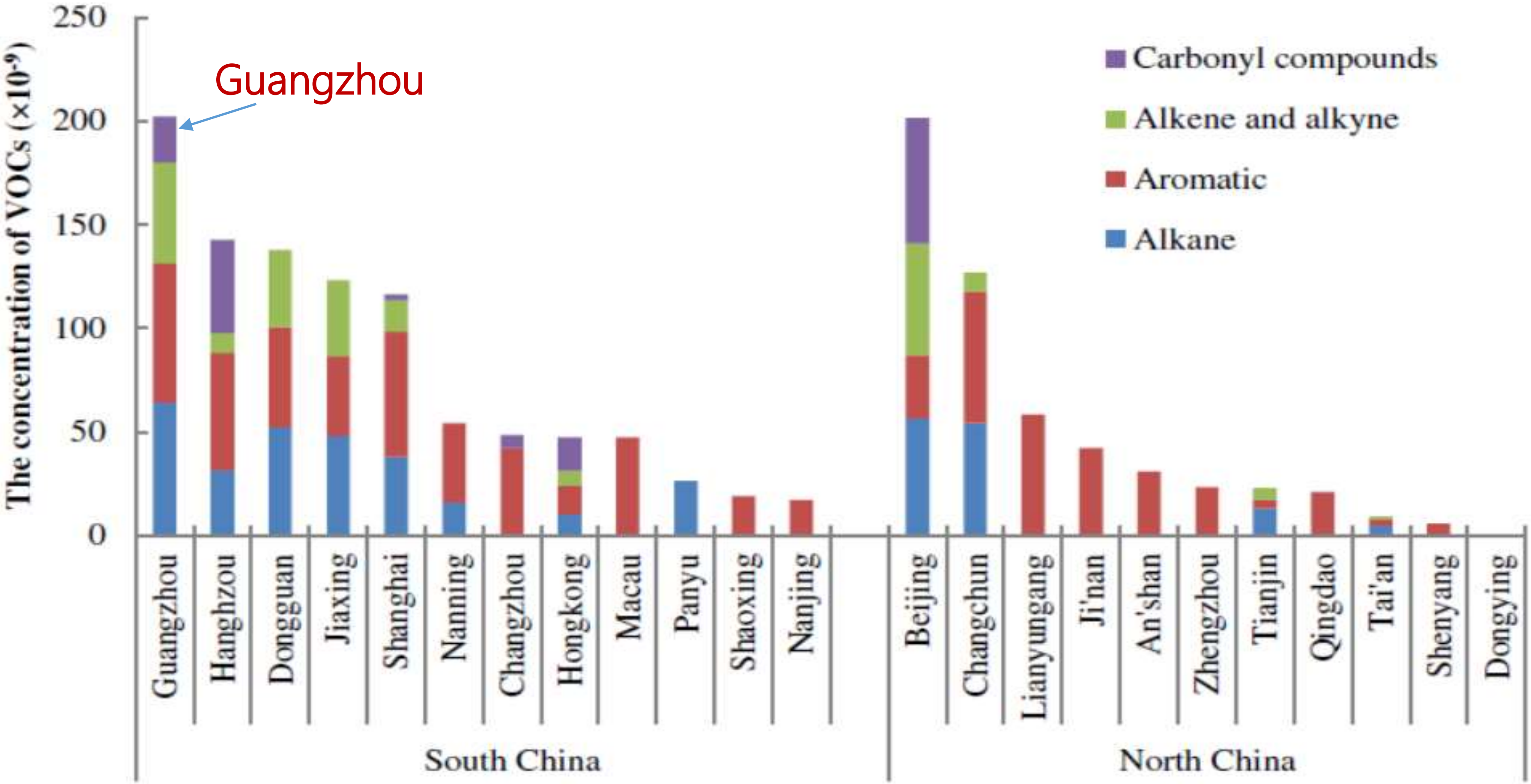


Fig. 1 – Spatial distribution of ambient volatile organic compounds in China.

Zhang et al. 2017. J. Environ. Sci.

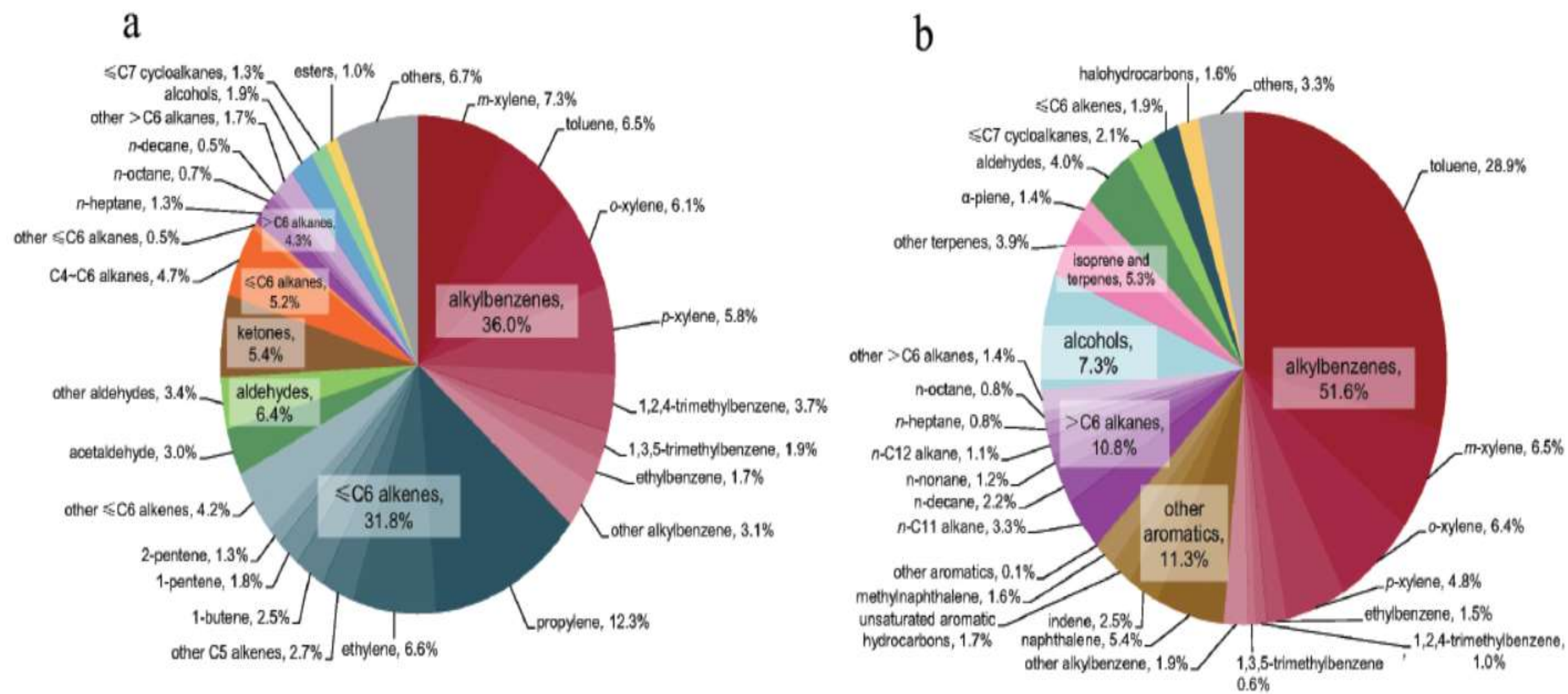
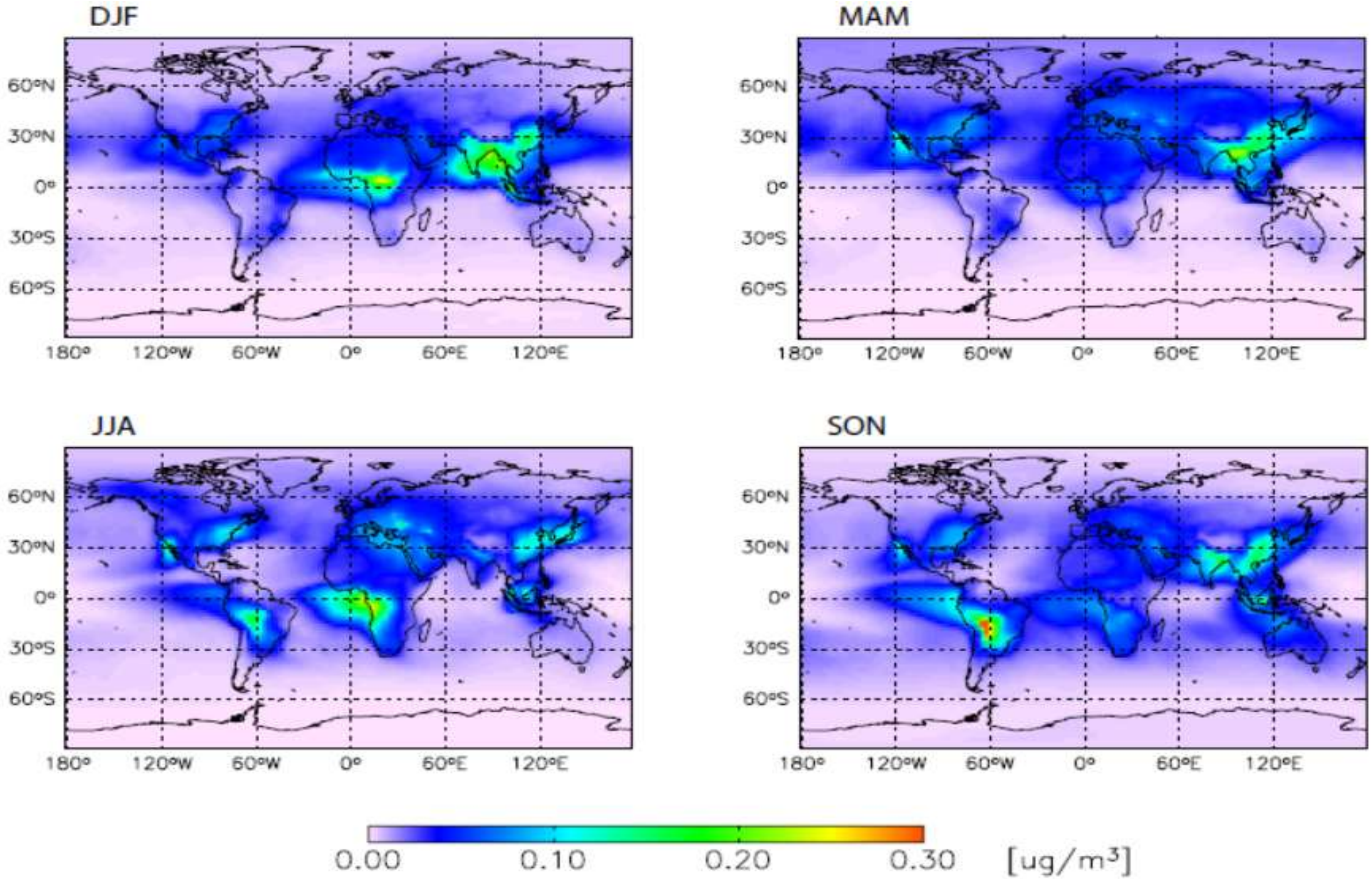


Fig. 2 – Contributions to (a) ozone and (b) SOA formation of major VOCs groups and individual VOCs species in China in 2010. SOA: secondary organic aerosol; VOCs: volatile organic compounds.

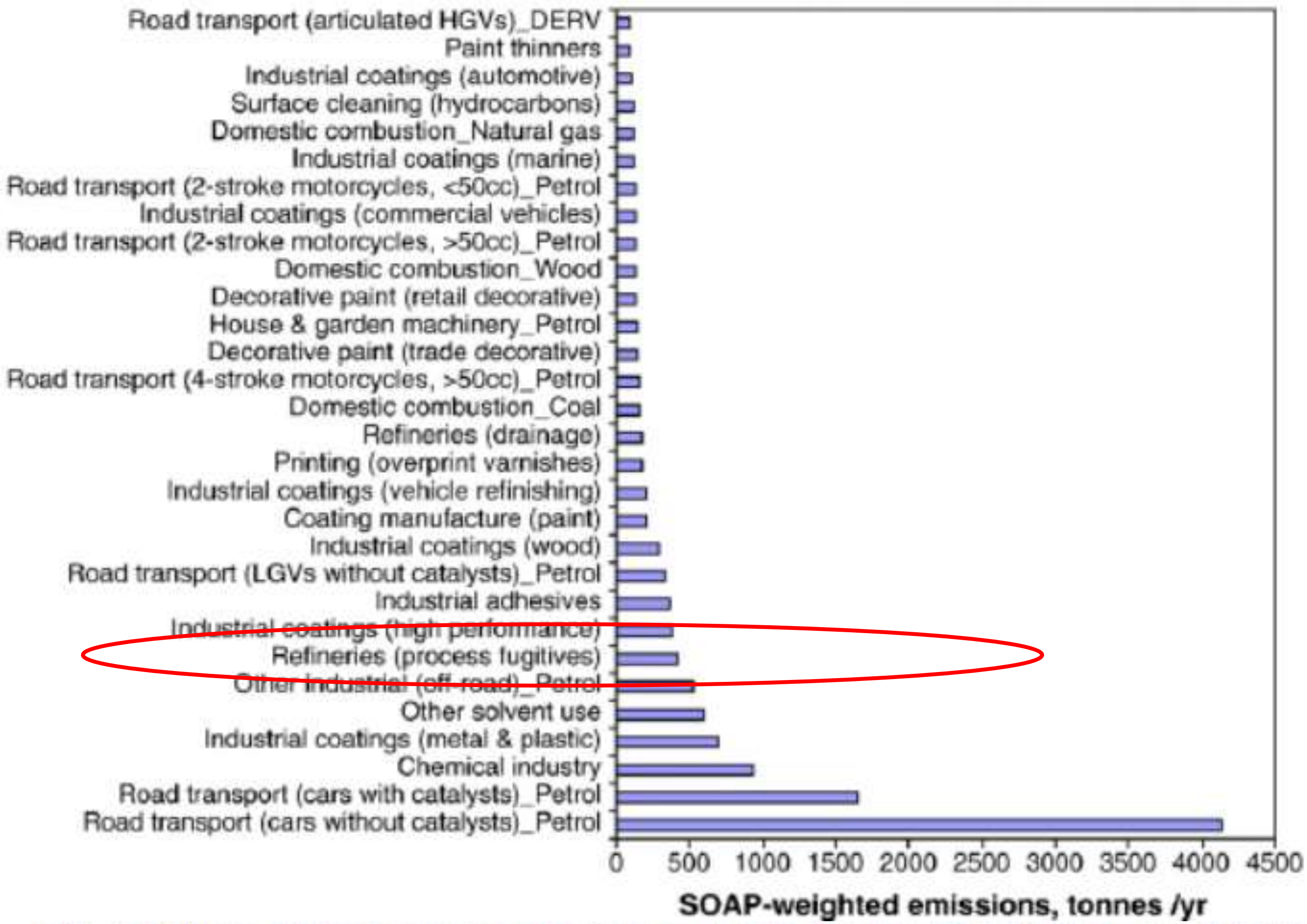
The SOA formation potential was calculated using the SOA yield method.

Aromatic SOA formation using GEOS-Chem Simulation



Seasonal distributions of the total surface-level SOA concentrations from benzene, toluene and xylene.

Henze, DK., et al. Atom. Chem. Phys. 2008, 8: 2405-2421.



SOAP-weighted mass emissions in tonnes (as toluene) per year from the 30 most prolific SOA forming sources in the UK.

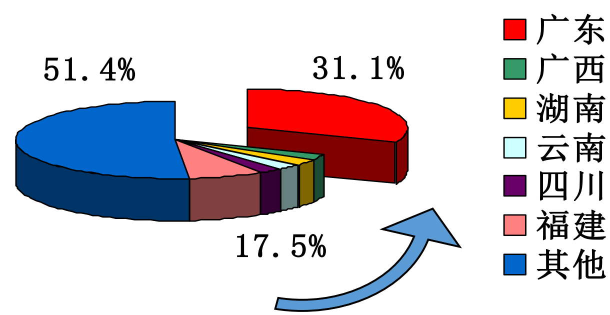
$$SOAP_i = \frac{Increment\ in\ SOA\ mass\ concentration\ with\ species,\ i}{Increment\ in\ SOA\ with\ toluene} \times 100$$

One of Great Challenges in China:
--how to reduce refinery VOC emissions

China

Guangdong

- **High level:** population, urbanization, industrialization
- **High production:** ≈ 1/3
- **High T:** more fugitive VOCs
- **High secondary pollutants:** O_3, SOA



- **Production：400 million tons，top 6**
- **Growth rate: oil (8%)；ethylene(20%)**
- **Distribution：coastal region**

（中石化年报；霍玉侠, **2011**）

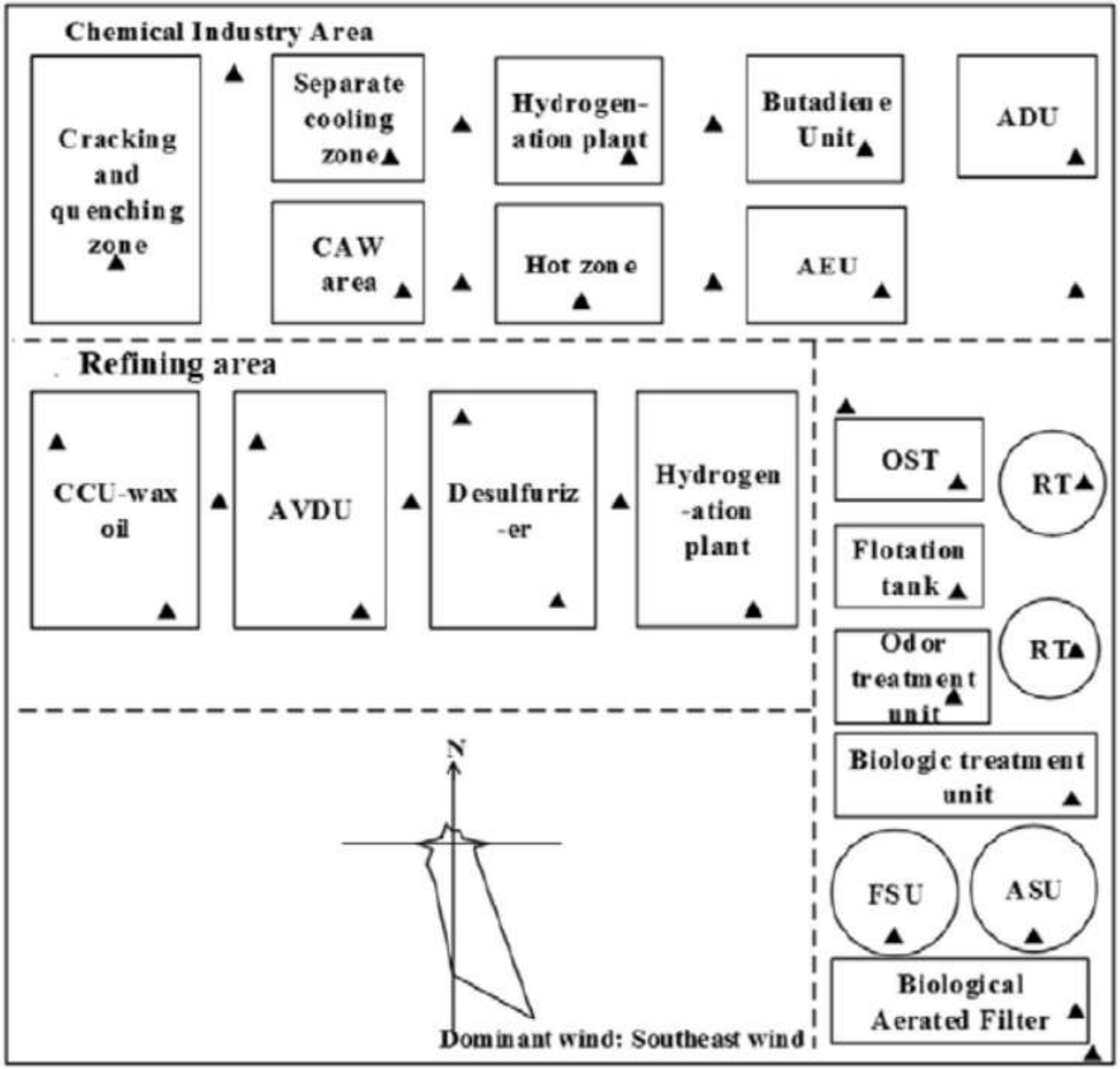
☞ **In this study, as a typical case study in Guangdong province, main object is to want to know the contribution of specific VOCs to SOA formation from Chinese refineries, and so that we may proposal the EPA to make scientific control policies.**

2.1 Schematic of sampling location

（1300万吨加工原油/年，1973年投产）

（1200万吨加工原油/年，2009年投产）

2.1 Schematic of sampling location



CAW: Compression in Alkaline Washing;
ADU: Aromatic Distillation Unit;
AEU: Aromatics Extraction Unit;
CCU: Catalytic Cracking Unit;
AVDU: Atmospheric and Vacuum Distillation Unit;
OST: Oil Separation Tank;
RT: Regulation Tank;
FSU: Flocculation and Sedimentation Unit;
ASU: Adsorption and Sedimentation Unit.

Zhang et al. 2017. Sci. Total Environ.

2.2 Three approaches selected

(1). FAC method

$$P_{FAC_i} = (VOC)_{i,0} \times FAC_i$$

where FAC_i is the fractional aerosol coefficient of species i (%), $(VOC)_{i,0}$ is the initial concentration of species i (μg m^{-3}). It should be noted that, since all the samples were obtained close to the major inner devices, the concentration of a measured VOC was regarded as the $(VOC)_{i,0}$.

(2). SOAP (toluene weighted mass contributions) method

$$SOAP_i = \frac{Increment\ in\ SOA\ mass\ concentration\ with\ species, i}{Increment\ in\ SOA\ with\ toluene} \times 100$$

SOAP values have been reported for a number of VOCs by Derwent et al (2010). There are 38 VOC species selected in this study.

$$P_{SOAP_i} = \frac{\sum (VOC_i \times SOAP_i)}{100} \times FAC_{toluene}$$

where $(VOC)_i$ is the mass contribution of a VOC source to species i (µg cm^{-3}) (linking with the molar mass of VOC species and based on the ideal gas law. We convert the unit of VOC species from ppbv to µg m^{-3}). $FAC_{toluene}$ is the fractional aerosol coefficient of toluene (%).

(3). SOA yield method

$$Y_{SOA_j} = \frac{\sum (X_{i,j} \times Y_{i,j})}{X_{TVOC}}$$

where j represents the five categories of VOC species; Y_{SOA_j} is the SOA yield of the petroleum refinery (unitless); $X_{i,j}$ is the weight percent (by carbon) of species i in each category j which can be identified by measurements (weight C%); $Y_{i,j}$ is the yield of species i in each category j (by carbon, unitless); X_{TVOC} is the weight percent (by carbon) of total identified SOA precursors and unidentified species (weight C%).

3.1 VOCs emission characteristics

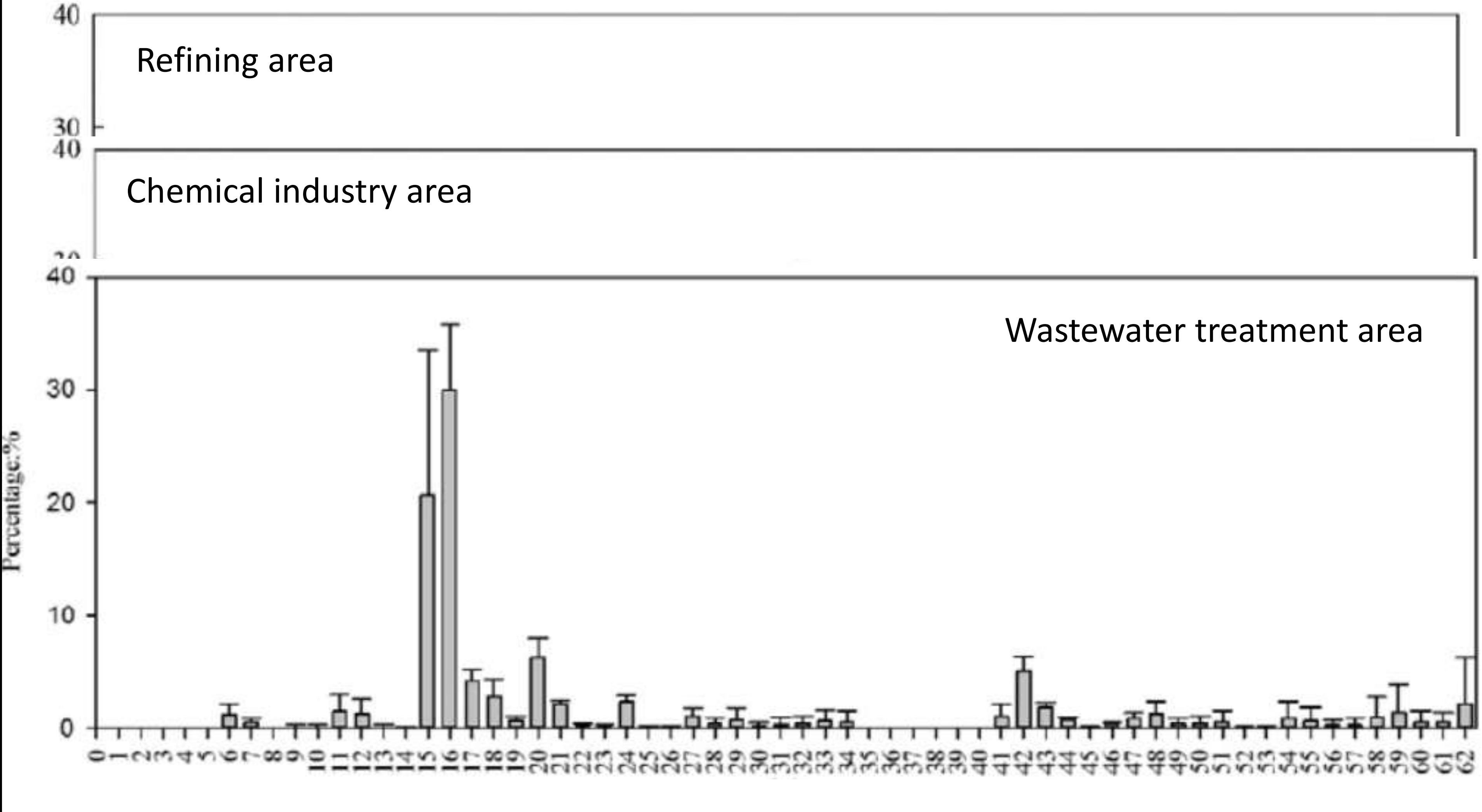


Fig. 3. Weight percent of VOCs emitted from the petroleum refinery.

15	2,3-dimethylbutane DL=0.003
16	2-methylpentane DL=0.005

Zhang et al. 2017. Sci. Total Environ.

3.2 FAC approach estimation

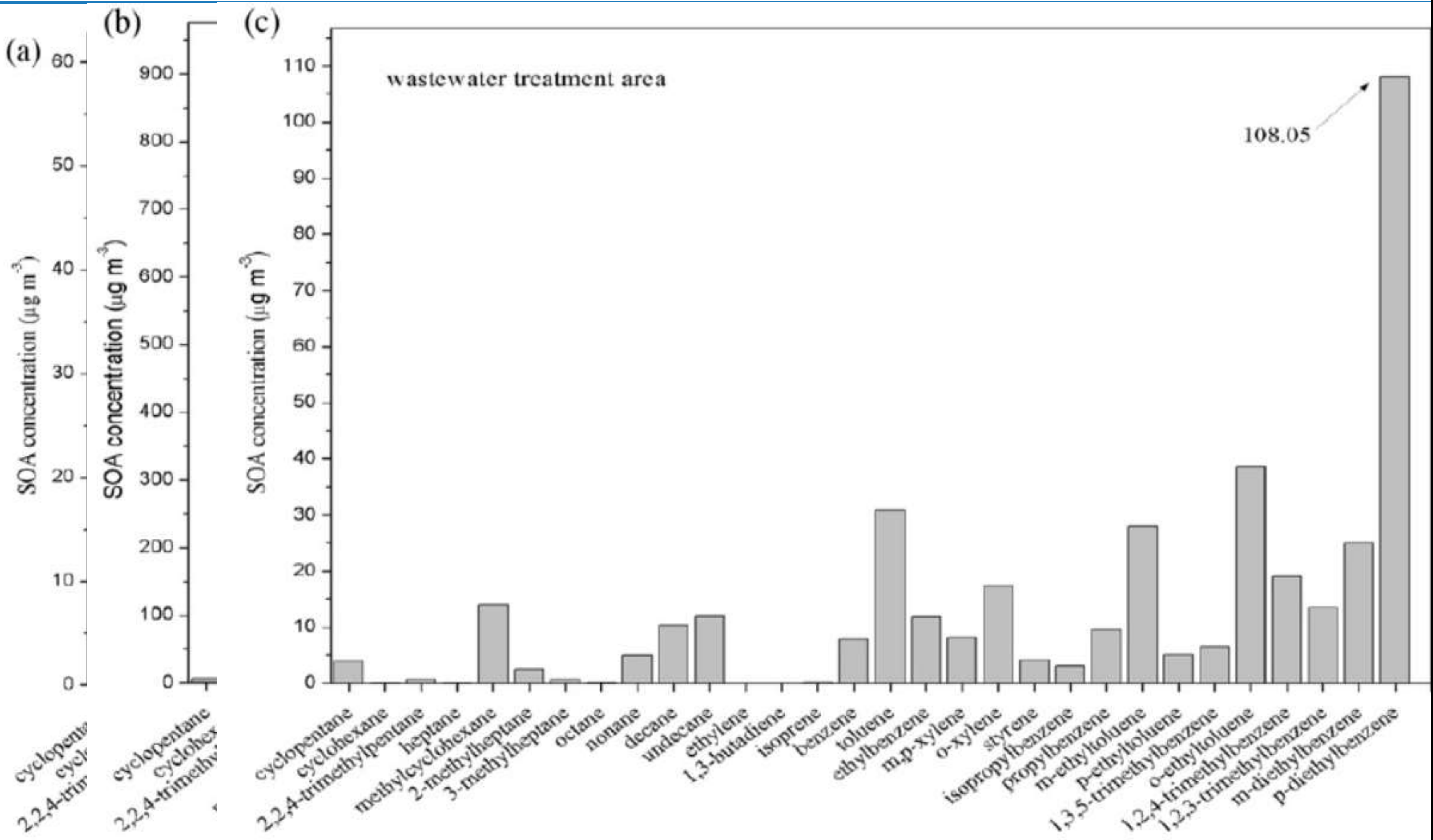


Fig. 5. SOA concentrations (in $\mu g \cdot m^{-3}$) predicted using FAC approach with measured VOCs concentrations.

Zhang et al. 2017. Sci. Total Environ.

3.2 FAC approach estimation

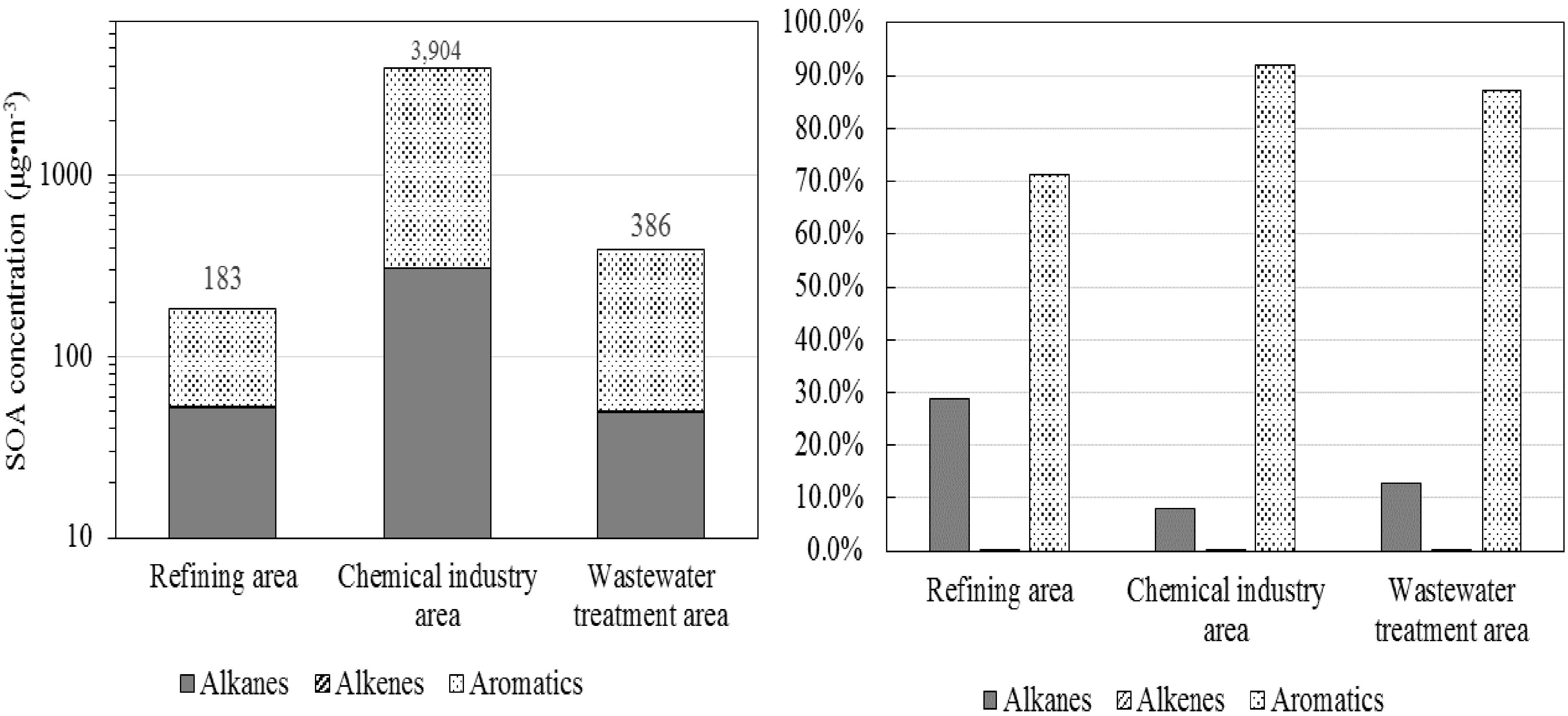


Fig. 6. (a) Total potential SOA concentrations predicted using FAC with measured VOCs concentrations. (b) Contributions of each VOCs species to the total SOA predicted using FAC with measured VOCs concentrations.

Zhang et al. 2017. Sci. Total Environ.

3.3 SOAP approach estimation

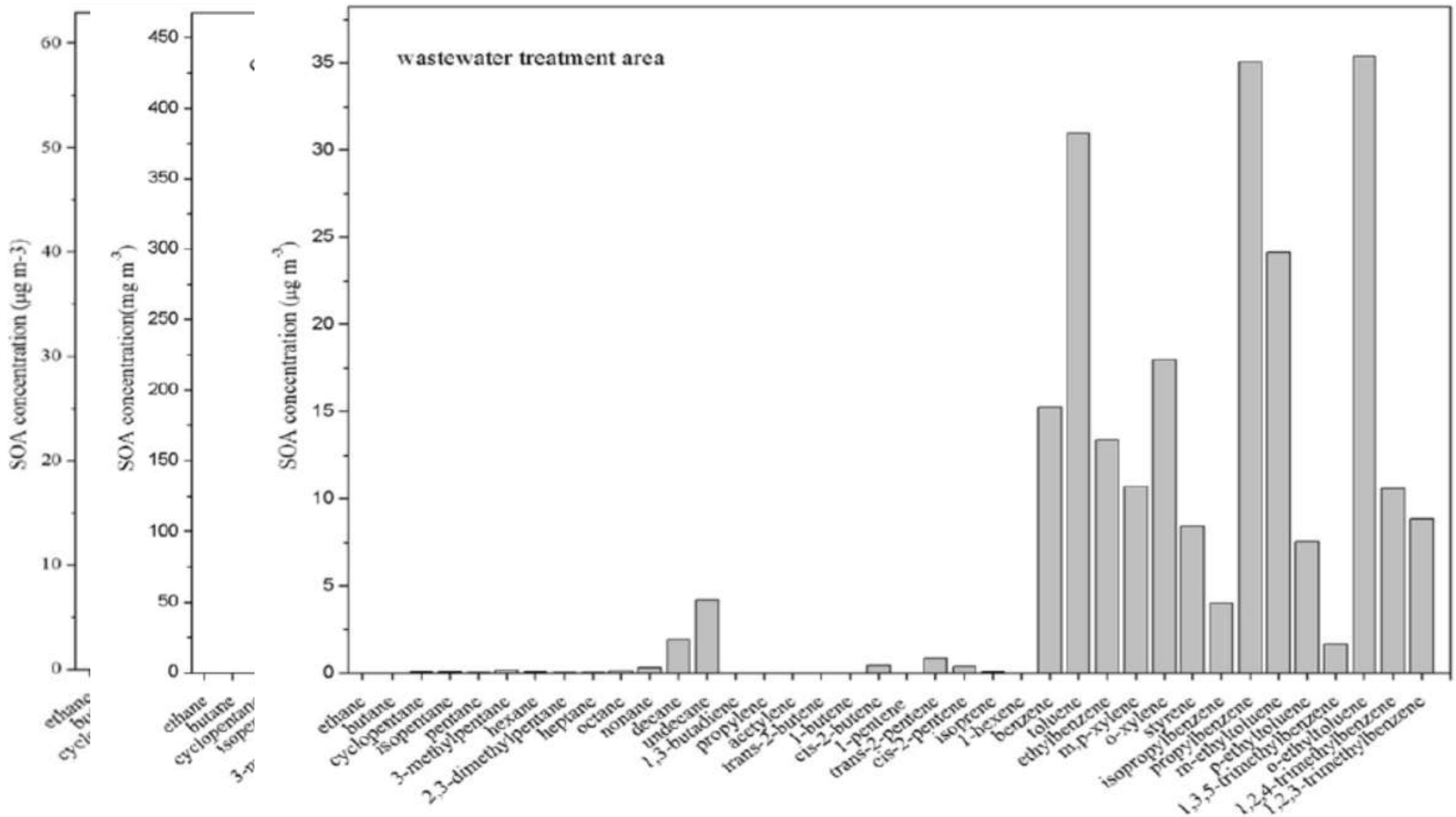


Fig. 7. SOA concentrations estimated from the VOCs emitted from the petroleum refinery using SOAP approach.

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3.3 SOAP approach estimation

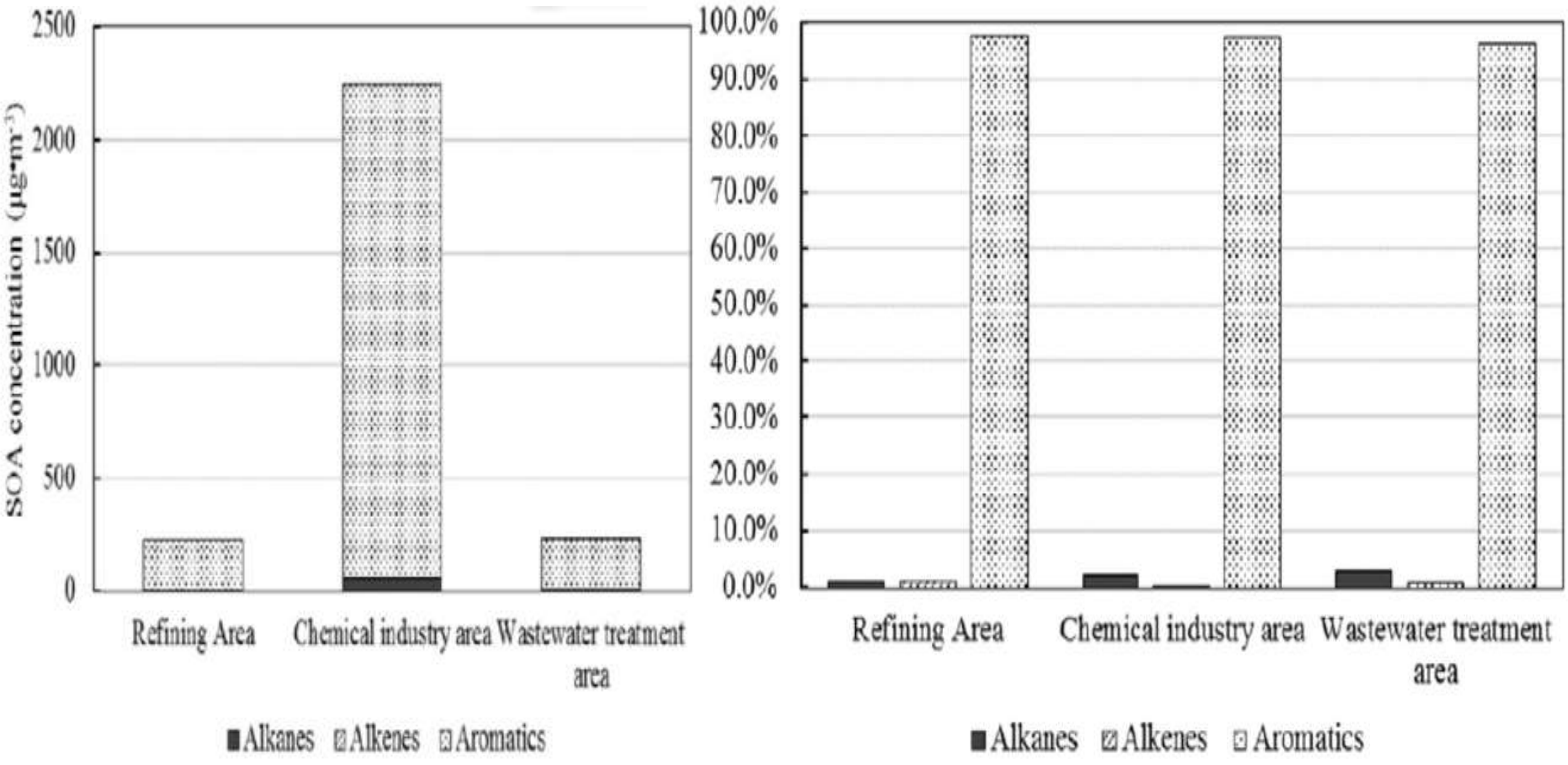

Fig. 8. (a) Total SOA concentrations estimated using SOAP approach (in μg•m^{-3}). (b) Contributions of each VOCs species to the total SOA concentrations using SOAP approach (%).

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3.4 SOA yield approach estimation

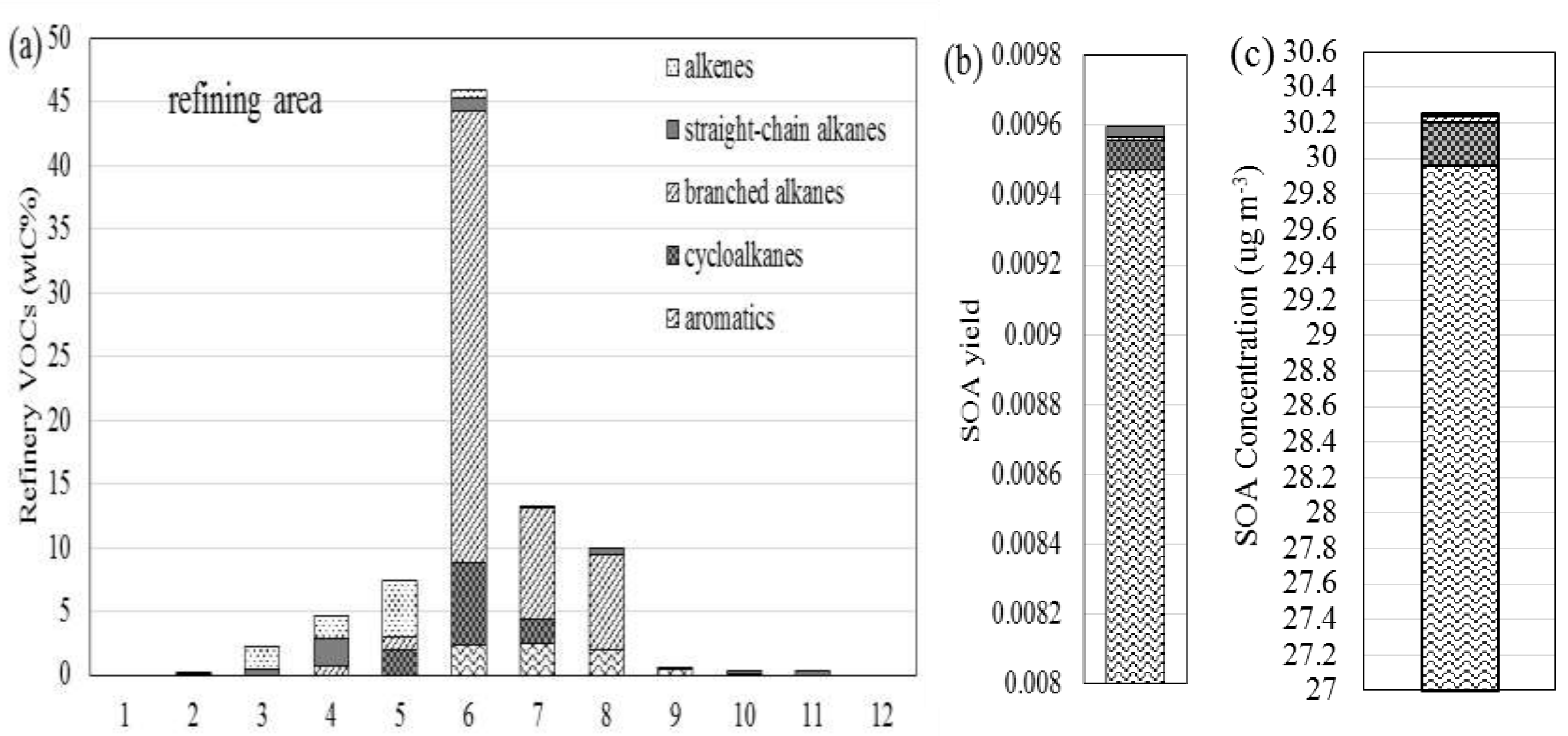

Fig. 6 (a) Distributions of mass by chemical class in carbon number of VOCs in the refining area; (b) calculated SOA yields based on C2-C12 VOCs; (c) calculated SOA concentrations based on C2-C12 VOCs.

3.4 SOA yield approach estimation

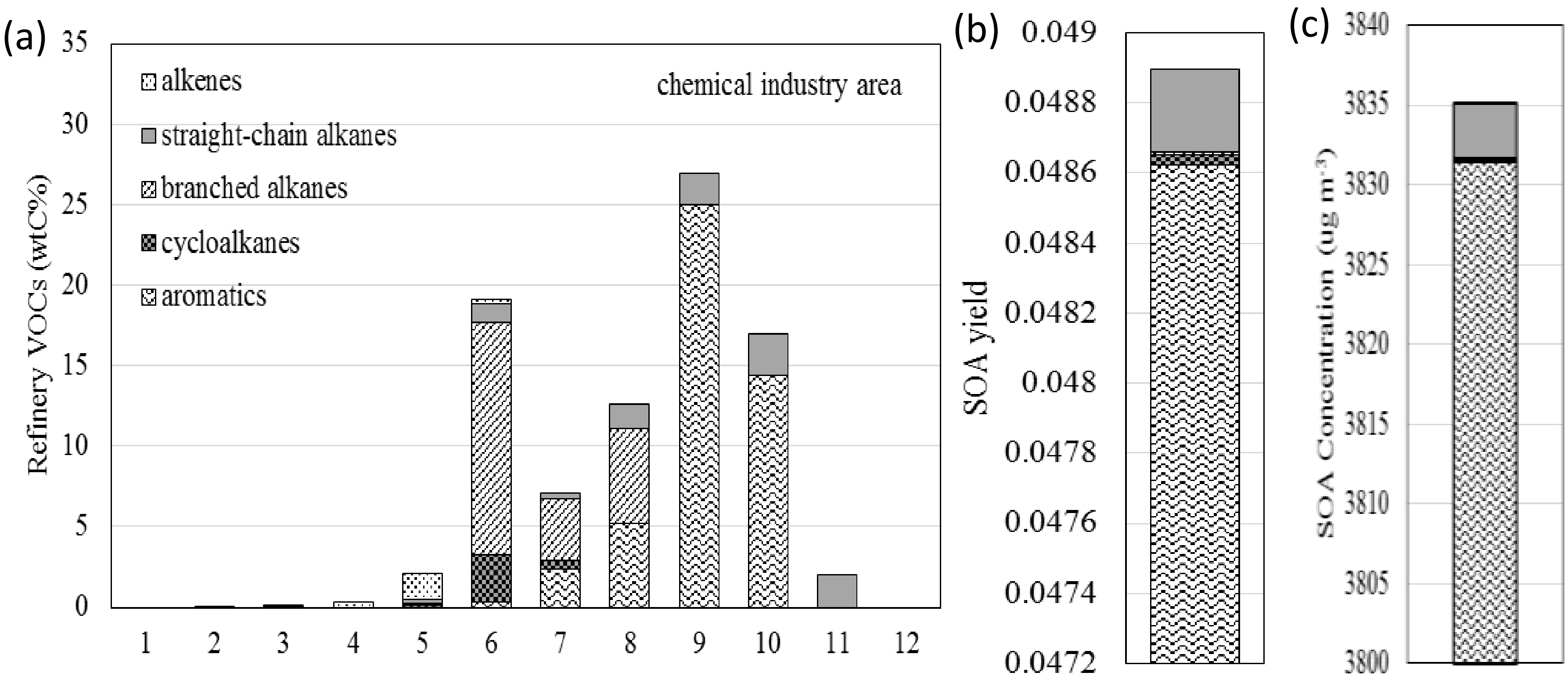

Fig. 6 (a) Distributions of mass by chemical class in carbon number of VOCs in the chemical industry area; (b) calculated SOA yields based on C2-C12 VOCs; (c) calculated SOA concentrations based on C2-C12 VOCs.

3.4 SOA yield approach estimation

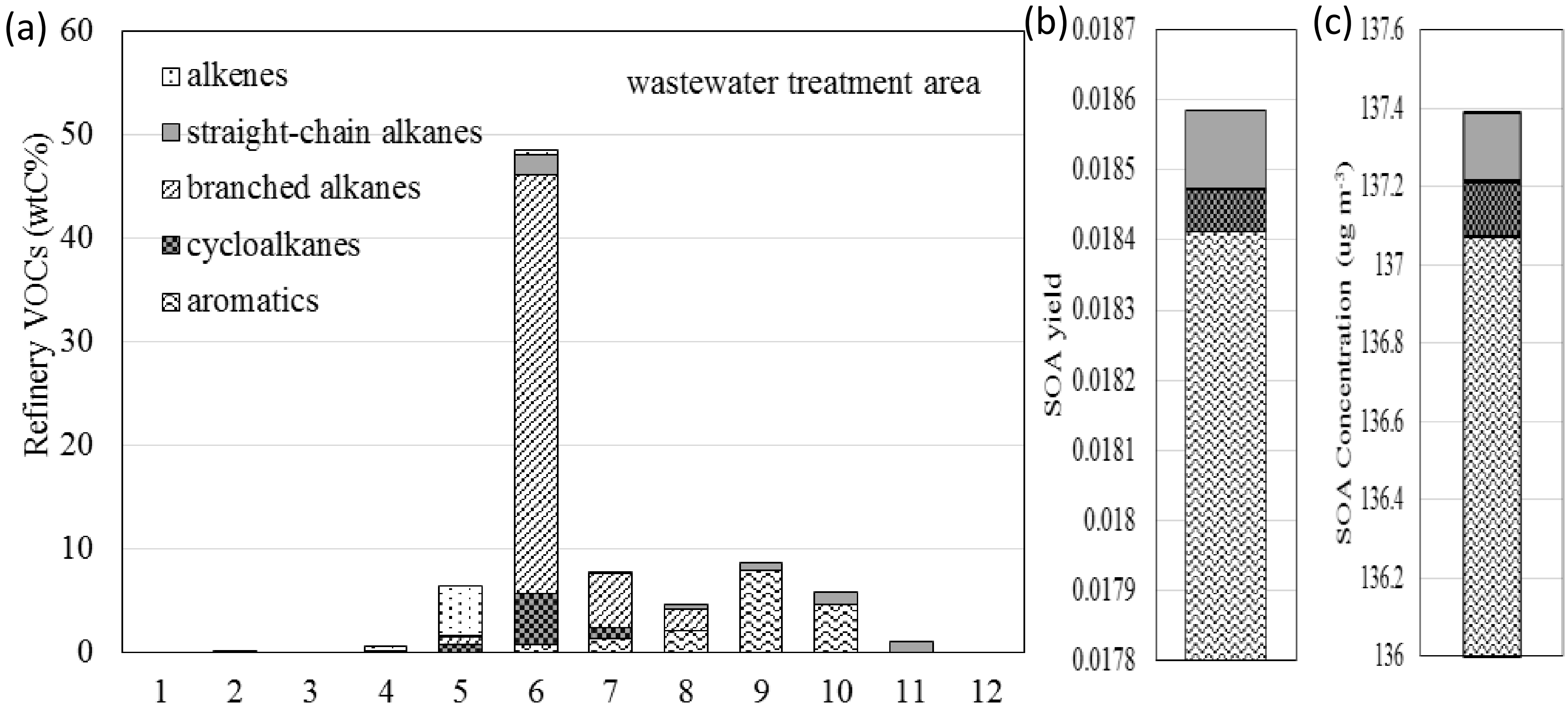

Fig. 6 (a) Distributions of mass by chemical class in carbon number of VOCs in the wastewater treatment area; (b) calculated SOA yields based on C2-C12 VOCs; (c) calculated SOA concentrations based on C2-C12 VOCs.

3.5 Total SOA concentration estimated using three approaches

Table 3. Total SOA concentration formed from petroleum refinery VOC emissions and the top five contributors

Parameters		refining area	chemical industry area	wastewater treatment area
FAC approach	SOA (μg m^{-3})	183	3,904	386
	Top five contributors	toluene, benzene, methylcyclohexane, ethylbenzene, m,p-xylene	p-diethylbenzene, m-diethylbenzene, o-ethyltoluene, m-ethyltoluene, toluene	p-diethylbenzene, o-ethyltoluene, toluene, m-ethyltoluene, m-diethylbenzene
SOAP approach	SOA (μg m^{-3})	222	2,245	233
	Top five contributors	toluene, ethylbenzene, benzene, m,p-xylene, o-xylene	o-ethyltoluene, propylbenzene, m-ethyltoluene, toluene, ethylbenzene	o-ethyltoluene, propylbenzene, toluene, m-ethyltoluene, o-xylene
SOA yield	SOA (μg m^{-3})	30	3,835	137
	Top five contributors	C_6-C_8 aromatics	C_9-C_{10} aromatics	C_9-C_{10} aromatics

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3.6 Comparison of three approaches

Approaches	Assumption	Drawbacks	Related VOC species
FAC	smog chamber exps (high NO_x and oxidant concentrations)	➢ loss of organic vapors onto chamber walls during the chamber experiments	only **30 VOCs** having FAC parameters
SOAP	photochemical trajectory model (PTM) (NO_x = 15 μg m^{-3})	➢ the SOAP parameters vary with background environmental conditions, particularly NO_x levels ➢ it use toluene as the index compound for the SOA formed	only **38 VOCs** having SOAP parameters, including 13 alkanes, 11 alkenes and 14 aromatic hydrocarbons
SOA yield	use gasoline and diesel exhaust as a priori information	➢ The SOA yield parameter is also dependent on the background environmental conditions, especially NO_x levels	only **27 VOCs** considered

✓ **SOA yield method:** considering the effect of molecular structures of VOCs species on the formation of SOA, and the initial conditions were used as a value relevant to chamber studies, urban areas, and downwind urban areas.

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Conclusion

- ✓ **By field measurement,** 61 VOC species were checked in a typical refinery in the PRD region, China,, and 2-methylpentane, 2,3-dimethylbutane were found among the most emitted VOCs from the whole refinery. However, for the refining and wastewater treatment areas, the three most abundant VOC species were all alkanes, and for the chemical industry area, *p*-diethylbenzene had the highest concentration.
- ✓ **By calculation,** the aromatics were found to contribute the largest proportion to the SOA formation potential. For the chemical industry area and wastewater treatment area, *o*-ethyltoluene, *m*-ethyl toluene and toluene were also among the top contributors, and for the refining area, toluene, benzene, ethyl benzene, and *m*,*p*-xylene were important as well.
- ✓ **By comparison,** the SOA yield method appears to be a better way and it is suggested to be used for the estimation of SOA formed from the VOC emissions.

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Team Members:

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