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Research article

Emission of volatile organic compounds (VOCs) from application of commercial pesticides in China

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ABSTRACT

Applying pesticides can result in emissions of volatile organic compounds (VOCs), but little is known about VOC emission characteristics and the quantities in particular regions. We investigated the use of pesticides in China based on a large-scale survey of 330 counties in 31 provinces and evaluated the national pesticide VOC emission potentials based on thermogravimetric analysis of 1930 commercial pesticides. The results showed that herbicides were the most extensively used pesticide category in China, accounting for 43.47%; emulsifiable concentrate (EC), suspension concentrate, and wettable powder were the dominant pesticide formulations, with proportions of 26.75%, 17.68%, and 17.31%, respectively. The VOC emission potential coefficient (EP) of the liquid formulations was higher than the solid formulations, and the maximum mean EP was 45.59% for EC and the minimum was 0.76% for WP. Among 437 high-VOC pesticide products used in China, EC accounted for 83.52%, and 16.93% of those contained abamectin. The total VOC emissions derived from commercial pesticides in China were 280 kt (kilotons) in 2018, and 65.35% of the contribution was derived from EC. Shandong, Hunan, and Henan were the three provinces with the highest pesticide VOC emissions (>21 kt/y). The emission rate of VOCs from pesticides was 24.80 t/d in China, which was higher than in San Joaquin Valley, California. These findings suggest that some comprehensive measures (e.g., perfecting pesticide management policy, strict supervision for pesticide production and use, and strengthening pesticide reduction publicity) should be taken to reduce VOC emissions from pesticide applications.

1. Introduction

A variety of environmental problems and extreme climate conditions are occurring more frequently (Curtis et al., 2017; Trevors, 2010), and the importance of protecting the environment to promote sustainable economic and social development has become increasingly prominent (Luna-Nemecio et al., 2020; Sundstrom et al., 2014). Air pollution and the greenhouse effect are significant environmental problems that must be solved jointly by all countries (Ramanathan and Feng, 2009; West et al., 2013). Reducing emissions of volatile organic compounds (VOCs) has been advocated because of their contribution to air pollution and the greenhouse effect (Chen et al., 2013; Jiang et al., 2021; Shao et al., 2009). Previous studies have demonstrated that emissions of some VOCs (e.g., formaldehyde, aldehyde, benzene, and toluene) directly induce short-term or long-term harm to human health (Lu et al., 2021; Reingruber and Pontel, 2018; Sarigiannis et al., 2011). VOCs are important precursors of ozone (O_3), secondary organic aerosols, and fine particulate matter ($PM_{2.5}$), which lead to haze, photochemical smog, and the greenhouse effect (Chang et al., 2009; Wu et al., 2017; Zheng et al., 2021). The complex atmospheric pollution characterized by $PM_{2.5}$ and O_3 is occurring increasingly more frequently in many Chinese cities (Gu et al., 2019; Kuerban et al., 2020; Luo et al., 2020). Therefore, controlling arbitrary emissions of VOCs from anthropogenic sources in China is important.

Industrial emissions are the main source of anthropogenic VOCs in the atmosphere of China (Wang et al., 2021; Yuan et al., 2022). The

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annual VOC emissions from industrial sources in China increased from 8777 kt (kilotons) to 12,446 kt from 2011 to 2018, with an average annual growth rate of 5.2% (Liang et al., 2020). Many studies have confirmed that the production and utilization of solvents is the main source of industrial VOCs (Lewis et al., 2020; Liang et al., 2019; Zhang et al., 2021). According to an estimate by the European Solvents Industry Group (ESIG), total VOC emissions from solvent sources in the European Union were 1981 kt/y in 2015 (Pearson, 2019). In China, VOC emissions from solvents accounted for 18% of total VOC emissions (just for anthropogenic, same as below) in the key provinces (Beijing, Tianjin, and Hebei) with air pollution (Li et al., 2019), while solvents volatilization contributed approximately 28% of total VOC emissions in the United States (USEPA, 2017).

A large number of solvents are applied during the production and use of pesticides (Guo et al., 2020; Siegel et al., 2017; Toose et al., 2015); thus, VOC emissions from this process cannot be ignored. In certain areas with heavy agricultural activities, pesticides have become a primary contributor to VOC emissions. For example, pesticides contributed approximately 5.5% of total VOC emissions to the San Joaquin Valley in 2019 (CDPR, 2019a; SJVAPCD, 2016). The California Department of Pesticide Regulation (CDPR) has been continuously monitoring the use of and VOC emissions from pesticides and has publicly released relevant reports since 1990 (CDPR, 2018; 2019b). Scholars in developed countries have conducted many studies on the applications of pesticides and their VOC emissions (Goodell, 2011; Kumar et al., 2011; Marty et al., 2010; Toose et al., 2015), and have mastered the local pesticide use structure and VOC emission characteristics. A few related studies in China have provided understanding about the pesticide-use patterns of Chinese farmers and the release of VOCs from a pesticide plant (Yang et al., 2019; Zhang et al., 2015). China ranked first for pesticide use and third for application intensity worldwide (OWD, 2021), but the national pesticide use structure and VOC emission profiles are unclear. A new study reported that the VOC regulations implemented recently by the Chinese government weakened the emission trends of anthropogenic non-methane VOCs (particularly in Chengdu and Dongguan) (Bauwens et al., 2022), but many government departments and industrial enterprises lack applicative and effective control measures specific to pesticide VOC emissions. Therefore, to guide the reduction in pesticide VOCs, it is necessary to systematically analyze the pesticide VOC emission characteristics and quantities in China.

The main objectives of this study were: (1) to investigate the application of commercial pesticides in China through a national survey; (2) to measure the VOC emission potentials of typical pesticides based on thermogravimetric analysis (TGA); (3) to further analyze the emission characteristics of pesticide VOCs from the aspects of different categories and formulations, and (4) to further estimate the VOC emission quantities of commercial pesticides in every provinces in China. The results of this study will provide new insight into the use structure and VOC emissions of pesticides in China, and help develop some effective measures to reduce pesticide VOC emissions.

2. Materials and methods

2.1. National survey on the application of commercial pesticides

Based on different farming systems, planting structures, pest types, and control methods, 330 representative counties were chosen from 31 provinces in China for a national survey on commercial pesticide application. The object county was designated from major crop-producing areas; 3–5 townships were chosen in each county, and 6–10 farmers who could reflect the local pesticide use levels were chosen in each township; each crop included at least 30 farmers. This survey was conducted from January 1 to December 31, 2018. The selected farmers registered the use of all pesticides (applied on all crops during the last year) in the Agri-Chemicals Management Information System (ACMIS, www.acmis.cn). For some cross-annual crops (such as winter wheat, rape, and potato), the pesticides used after crop-planting in the autumn or winter of 2017 were combined into the total use of pesticides during the harvest year (2018), while only the use of pesticides in 2018 was counted for perennial fruit trees and vegetables.

2.2. Collection of commercial pesticide samples

The registration rate of fumigants by the end of May 2021 was only 0.0093% ($n_{total} = 42996$, excluding those that expired before 2018) in the ACMIS of China (CPIN, 2021), so fumigants were not considered in this study, and all commercial pesticides collected were non-fumigants. Taking the use rank of commercial pesticides in 2018 as the reference, a variety of representative commercial pesticides were purchased from the agricultural materials markets (Hunan, Hubei, Jiangsu, Zhejiang, Henan, and other provinces), online sales markets, pesticide production enterprises, and other channels. To facilitate the search for samples, verification, and testing records, all collected pesticides were assigned a unique sample number based on the ACMIS registration number.

The formulation of a pesticide has a strong effect on the volatile potential of the VOCs (Kumar et al., 2011; Toose et al., 2015; Zeinali et al., 2011); thus, the coverage and proportion of the pesticide formulations were the main factors considered before collecting the samples. According to the formulation proportions from the 2018 survey results and the registered proportions in the ACMIS, the study set sampling proportions of the different formulations was 26% for emulsifiable concentrate (EC), 20% for wettable powder (WP), 16% for suspension concentrate (SC), 9% for aqueous solutions (AS), 6% for water dispersible granule (WG), and oil dispersion (OD), 5% for emulsion (oil in water) (EW), 3% for micro-emulsion (ME), and granules (GR), 2% for water soluble powder (SP), other liquid formulations (OLF), and other solid formulations (OSF), respectively. The application range of the pesticides covered the main cereal crops, vegetables, fruits, and common flowers, trees, and grasses (314 species), which are widely grown in all provinces of China. Some pesticides could not be obtained in the short term, but 9 common pesticide types and 27 pesticide formulations were collected. In total, this study collected 1930 representative pesticides, of which 1592 pesticides were on the list of pesticides investigated in 2018, and 851 pesticides were in the top 3000 ($n_{total} = 11{,}271$) of use rank of investigation; The use of the 1592 pesticides accounted for 40.23% of total use.

2.3. Measurement of the VOC emission potential coefficients of commercial pesticides

The VOC emission potential coefficients (EP) were calculated based on the thermal mass loss (TM) and moisture content (MC) of the pesticide products according to the method in the CDPR (CDPR, 2005). The TM values of the pesticide samples were measured by TGA as a CPDR method (CDPR, 2005) and in related reports (Toose et al., 2015; Zeinali et al., 2011). The MC values of the pesticide samples were measured using Karl Fischer coulometric titration according to the water testing method in pesticides (GB/T1600-2001) from China (NSTCP, 2001). Each pesticide product was determined in triplicate, and the details of the detection methods are described in Text S1 and Text S2. The *EP* value (%) of collected pesticide products was corrected using the formula:

$$EP = \overline{TM} - \overline{MC} \tag{1}$$

where $\overline{TM}$ represents the average thermal mass loss (%) for three replicate samples; $\overline{MC}$ is the average moisture content (%) for three replicates. If $\overline{MC} > \overline{TM}$ caused the value of EP to be negative, then the EP value is 0.

2.4. Estimate of VOC emissions from applying commercial pesticides in China

According to the CDPR method, the annual VOC emission inventory for pesticides was estimated by multiplying the EP value by total use and the application method adjustment factor (AMAF) (CDPR, 2005). The AMAF is not available for most non-fumigants, and is assumed to be 1, namely the entire volatile fraction is emitted into the atmosphere in a worst-case scenario (Zeinali et al., 2011). In this study, taking each province as a calculated unit, the VOC emissions from commercial pesticides were estimated using the following formulas:

$$E_F = U_F \times \overline{EP_F} \tag{2}$$

$$U_F = U_C \times f_F \tag{3}$$

where E_F represents the VOC emissions (t/y) of a particular formulation; U_F represents the use amount (t/y) of this formulation in a particular province in 2018; $\overline{EP_F}$ is the average VOC emission potential coefficient (%) of the formulation; U_C is the use amount (t/y) of the commercial pesticide in a particular province in 2018, which was cited from the China Rural Statistical Yearbook (2019) (NBSC, 2019), and f_F is the national use percentage (%) of this formulation obtained during the 2018 investigation.

The sum of the VOC emissions from the different formulations in a particular province was the total VOC emissions of commercial pesticides in the province, while the sum of VOC emissions from commercial pesticides in the 31 provinces was regarded as the total VOC emissions of commercial pesticides from the Chinese mainland.

3. Results and discussion

3.1. Commercial pesticide use in China

According to the survey results, the use of different pesticide categories and formulations in 2018 is shown in Fig. 1a and b and Tables S1–S2. The survey involved 28,803 peasants from 330 representative counties in 31 provinces. The number of commercial pesticides

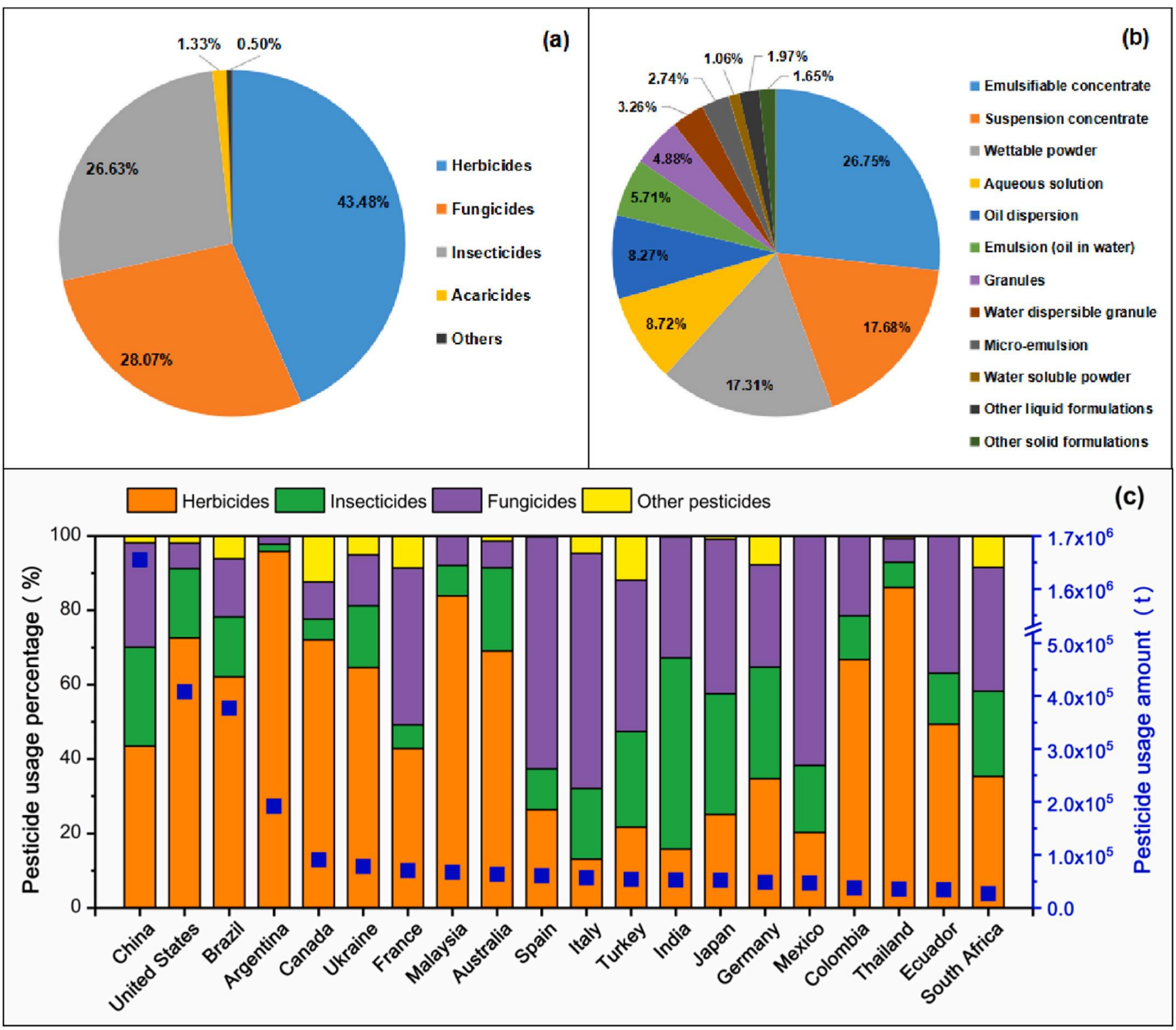

Fig. 1. (a) and (b) Use structure of commercial pesticides for different categories and formulations in China; (c) Use structure comparison of commercial pesticides for different categories in the top 20 countries.

used was 11,271, and the amount of these commercial pesticides used was 812,305 kg in 2018 (Tables S1–S2). Among them, the use percentages of herbicides, fungicides (including bactericides), insecticides, acaricides, and other categories were 43.47%, 28.07%, 26.63%, 1.33%, and 0.50%, respectively (Fig. 1a), while the use percentages of the different formulations, including EC, SC, WP, AS, OD, and EW were 26.75%, 17.68%, 17.31%, 8.72%, 8.27%, and 5.71%, respectively, with the use percentages of the other formulations were <5% (Fig. 1b). These survey data indicate that herbicides were applied more extensively than other pesticide categories, and the EC, SC, and WP were the dominant pesticide formulations. In general, pesticide use structure is mainly affected by the weeding method, planting structure, pest species, and production technology of the pesticide.

To our knowledge, this is the first report on the integrated pesticide use structure (classified by type or formulation) in China based on a large-scale survey. A previous study (Gu, 2017) reported that the registration percentages of insecticides, fungicides, and herbicides were 39.98%, 25.62%, and 24.11% (total 35,604) at the end of 2016. The present study also calculated the registration percentages: 35.78% for insecticides, 25.85% for fungicides, and 26.54% for herbicides (total 42, 992), which were similar to the above-reported results, but different from the practical applications (see Fig. 1a). For example, insecticides were the most registered, but herbicides were the most used. Due to rarely applicable crops, poor efficacy, fierce competition, and inappropriate marketing mode, some of the registered pesticides were applied in a narrow scope and were not involved in the 2018 national survey. Therefore, the registration percentages of the pesticides do not accurately reflect their actual application.

Herbicides, fungicides, and insecticides are the most widely used pesticides on a global scale, and their use percentages were 25.10%, 12.06%, and 7.50% in 2014 (Zhang, 2018). Herbicides were the most commonly used pesticides from 1990 to 2017 (OWD, 2021). According to the pesticide use amount of different countries in 2016 or 2017 (OWD, 2021), the top 20 countries were sorted to compare the pesticide use structure, and the results are shown in Fig. 1c and Table S3. China used more pesticides than any other country and 4 times more than the country used the second most (United States). Because of the diversity of the planted crops, pesticide application methods, and climatic conditions, the pesticide use structure of the top 20 countries was different. To be specific, the pesticide type most commonly used (>50%) in 9 of 20 countries (United States, Brazil, Argentina, Canada, Ukraine, Malaysia, Australia, Colombia, and Thailand) was herbicides, while for 3 of 20 countries (Spain, Italy, and Mexico) was fungicides and insecticides for India. The remaining 7 countries (including China) have a relatively balanced pesticide use structure. These analyses suggest that China is truly the largest pesticide user, even though its pesticide use structure is relatively balanced; applying a pesticide in China may emit more VOCs than in any other country.

3.2. VOC emission potential analysis for representative commercial pesticides

3.2.1. MC, TM, and EP values and their interrelationships

Representative commercial pesticides (n = 1930) were collected to systematically assess their VOC emission potentials by detecting MC, TM, and EP, and the results are summarized in Table 1 (detailed list in Table S4). The MC, TM, and EP values for the different pesticide formulations were different. The MC values for all pesticide samples presented a wide range (0–91.87%), and their mean values ranged from 1.16% to 56.71%. Among them, the mean values for five liquid formulations (SC, AS, EW, ME, and OLF) ranged from 38.28% to 56.71%, and the others were <5.2%. Similarly, the TM values for all pesticide samples varied from 0.04% to 99.72%, and their mean values were divided into two categories: 1) 50.06–69.44%, including six liquid formulations (EC, SC, AS, EW, ME, and OLF); 2) 3.22–11.77%, including five solid formulations (WP, WG, SP, GR, OSF) and OD. The pesticide formulation with the highest EP value usually demonstrates strong VOC emission potential (Zeinali et al., 2011; Zhan and Zhang, 2012). The formulations with a high VOC emission potential were all liquids, and their average EP values were in the order of: EC (45.59%) > ME (28.72%) > EW (24.63%) > OLF (17.85%) > OD (10.61%) > SC (10.08%) > AS (9.26%), while those for the solid formulations were OSF (7.79%) > GR (2.99%) > WG (1.19%) > SP (0.77%) > WP (0.76%). The correlations between the TM, MC values and the EP value for typical pesticide formulations (n ≥ 84) were analyzed to explore the relationship between the formulations and VOC volatilization, and the analysis results are described in Text S3, and shown inFig. S1 and Fig. S2.

3.2.2. Distribution characteristics of the EP values

The distribution characteristics of the EP values for typical pesticide formulations (n ≥ 84) were analyzed based on cumulative frequencies, and the results are shown in Fig. 2. The distribution of the EP values for EC (n = 536) was very homogeneous between the range of 0–100%, and was almost a straight line (Fig. 2a), indicating that their VOC emission potential was significantly different. The EP values for SC (n = 280) mainly gathered in the range of 0–35%, and 89% of the EP values were <20% (Fig. 2b). Similarly, 88% of the EP values for AS (n = 143) were <20%, and 29% of the EP values were zero (Fig. 2c). None of the EP

Table 1
Summary of moisture content (MC), thermal mass loss (TM), and emission potential coefficient (EP) values for different pesticide formulations (n_{total} = 1930).

Pesticide formulation	Formulation abbr.	Sample number	Moisture content (MC, %)			Thermal mass loss (TM, %)			Emission potential coefficient (EP, %)		
			Range	Median	Mean	Range	Median	Mean	Range	Median	Mean
Emulsifiable concentrate	EC	n = 536	0.00–88.26	0.72	4.51	0.48–99.72	50.70	50.06	0.00–98.88	46.62	45.59
Suspension concentrate	SC	n = 280	0.40–91.27	58.30	55.78	2.49–99.42	67.25	65.45	0.00–84.90	7.68	10.08
Aqueous solution	AS	n = 143	0.41–91.87	55.55	56.71	27.54–99.27	62.61	64.63	0.00–87.83	2.82	9.26
Emulsion (oil in water)[a]	EW	n = 88	0.24–87.61	32.33	38.28	18.85–96.17	59.23	62.91	2.36–63.03	25.06	24.63
Oil dispersion	OD	n = 86	0.14–5.98	0.83	1.16	0.75–64.25	7.85	11.77	0.02–64.05	6.41	10.61
Micro-emulsion	ME	n = 84	0.16–90.90	45.92	40.74	4.66–97.69	75.20	69.44	0.00–68.29	29.09	28.72
Other liquid formulations[b]	OLF	n = 49	0.21–89.16	44.84	44.43	12.75–95.65	64.60	62.01	0.00–76.54	7.78	17.85
Wettable powder	WP	n = 431	0.14–12.94	2.50	3.16	0.04–30.02	2.47	3.22	0.00–22.58	0.00	0.76
Water dispersible granule	WG	n = 136	0.57–16.12	3.94	5.18	0.60–23.81	5.05	5.91	0.00–9.99	0.58	1.19
Water soluble powder	SP	n = 39	0.65–13.37	3.30	3.67	0.25–11.31	2.55	3.48	0.00–10.26	0.00	0.77
Granules[c]	GR	n = 32	0.46–12.21	2.41	3.26	0.27–32.17	2.97	5.72	0.00–27.95	0.92	2.99
Other solid formulations[d]	OSF	n = 26	0.28–20.92	2.22	3.77	0.09–61.73	3.75	11.36	0.00–59.58	0.74	7.79

[a] Containing emulsion for seed treatment (n = 1).
[b] Including soluble concentrate (n = 16), capsule suspension (n = 13), suspo-emulsion (n = 9) and flowable concentrate for seed treatment (n = 11).
[c] Including granule (n = 14), fine granule (n = 2), water soluble granule (n = 15) and effervescent granule (n = 1).
[d] Including technical material (n = 13), crystal (n = 1), crystal powder (n = 1), dustable powder (n = 3), effervescent tablet (n = 1) and seed treatment solid formulations (n = 7).

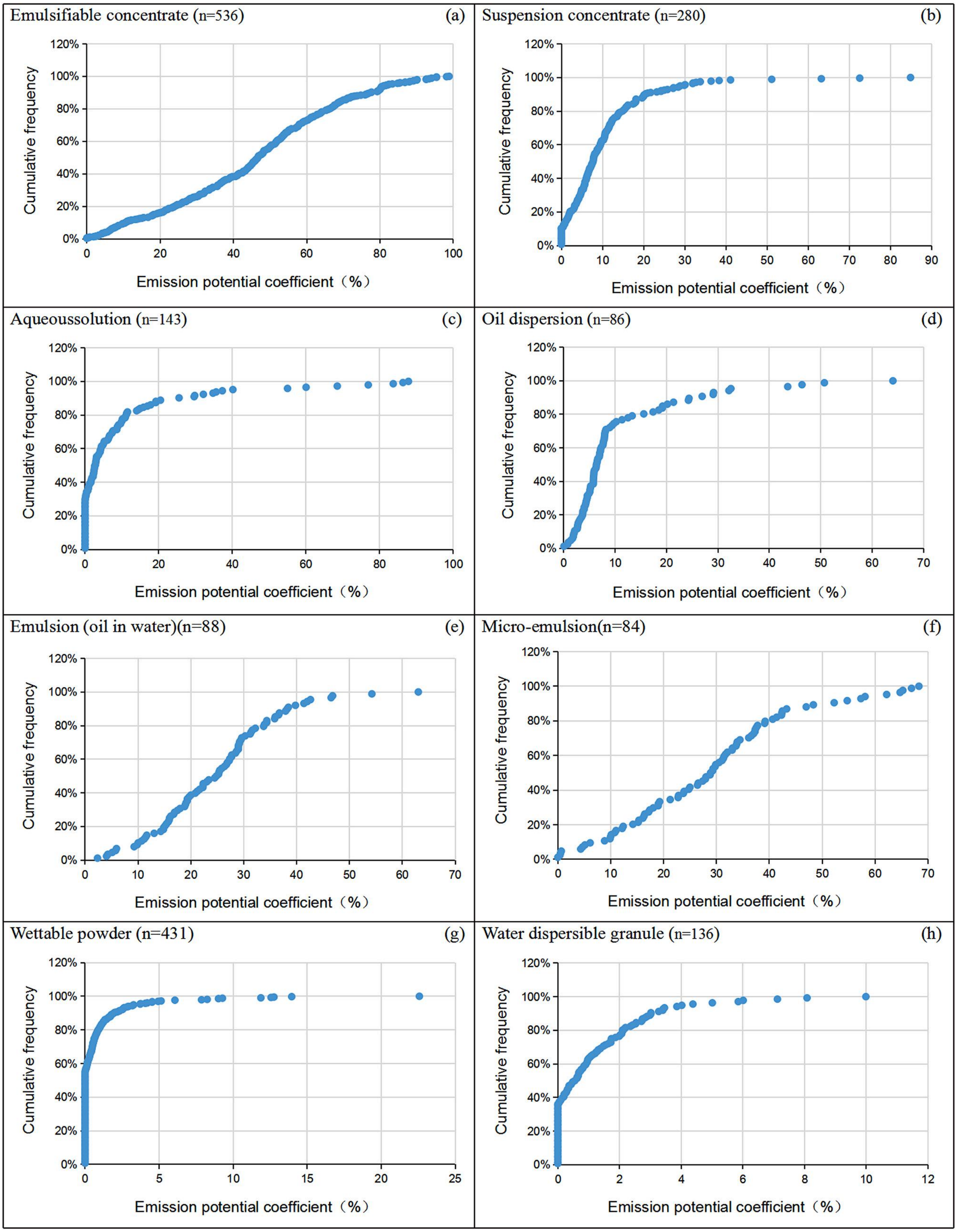

Fig. 2. Distribution diagram of the cumulative frequencies for representative pesticide formulations.

values for OD (n = 86) were equal to zero, and 80% of the EP values were <16% (Fig. 2d). The EP values for EW (n = 88) and ME (n = 84) varied from 0 to 70%, but most were <40% (Fig. 2e and f). For the solid formulation WP (n = 431), 55% of the EP values were zero, and the remainder were <14% except for the maximum of 22.58% (Fig. 2g), indicating that WP had a weak VOC emission potential, and 55% of the WP did not release VOCs. A similar phenomenon was observed for another solid formulation WG (n = 136), the EP values were <10%, and 36% of the values were zero (Fig. 2h). The above results suggest that the VOC emission potential of the liquid formulations was significantly higher than that of the solid formulations.

3.2.3. Comparison of the EP values with related reports

Few studies have reported EP values for pesticides at home and abroad. Based on the limited reports, the EP values of typical pesticides (specific to active ingredients) were selected for comparison with this study, and the results are shown in Table S5. Compared to the report of Zhan and Zhang (2012), in which the mean EP values of some of the active ingredients were similar to those of the present study, including abamectin, azoxystrobin, chlorpyrifos, iprodione, and lambda-cyhalothrin. The mean EP values of cypermethrin, carbendazim and glyphosate in the present study was different from the EP guideline values pubilshed by the Ministry of Ecology and Environment (MEE) of the PRC (MEE, 2014). The differences in the sample number of pesticides and the solvents used may be responsible for the differences in EP for the same active ingredient. Previous studies have verified that the solvent type used in the pesticide formulation is a primary cause which affects the VOC volatile potential (Kumar et al., 2011; Toose et al., 2015; Yates et al., 2011). Furthermore, the EP values of typical active ingredients were compared between the CDPR (CDPR, 2021) and the present study based on the classification of low-VOC and high-VOC pesticide products. Some similar mean EP values were found for abamectin and oxyfluorfen, regardless of low-VOC or high-VOC (excluding no data), while significant differences were found for chlorpyrifos, but it was inconclusive due to the low number high-VOC samples for CDPR (n = 1) or low-VOC in this study (n = 2). The EP values measured in this study are very close to other reported values in cases of a high sample number.

3.2.4. High-VOC pesticide products in China

According to the CDPR report (CDPR, 2021), the maximum EP threshold (%) of high-VOC pesticides was 35% in the most lenient scenario. This study analyzed the distribution of high-VOC pesticide products (EP > 35%) in China to provide a reference for avoiding high-VOC pesticide products and alternative high-VOC solvents (summarized in Table 2). In total, 437 high-VOC pesticide products were selected from the 1930 pesticide products. The number proportion of high-VOC pesticide products was in the order of insecticides (52.40%) > herbicides (32.72%) > fungicides (10.30%) > other pesticides (4.58%), and their mean EP values ranged from 50.86% (fungicides) to 60.54% (insecticides). EC accounted for 83.52% of high-VOC pesticide products, with a higher mean EP (58.29%) than most formulations; while the number proportion of the other formulations was 0.23–5.95%, with a mean EP of 35.54–68.15%. Notably, all liquid formulations accounted for 99.54% of the high-VOC pesticide products, while solid formulations (technical material) only accounted for 0.46%, and frequently used WP (solid) was not found in the high-VOC pesticide list. Sixteen active ingredients (top 10, including parallel cases) were selected from the high-VOC pesticide list based on the product number rank. The active ingredients with the highest mean EP were imidacloprid (70.20%), followed by beta-cypermethrin (69.38%), while those with low mean EPs were isoprothiolane (47.74%) and prochloraz (48.63%). In total, sixteen active ingredients accounted for 71.85% of the high-VOC pesticide products. The active ingredient with the highest proportion was abamectin (16.93%), suggesting that high-VOC pesticide products containing abamectin are commonly used in China, as in California, USA

Table 2
Distribution situation of emission potential coefficient (EP) for the pesticide products with high-VOC emission (n_{total} = 437).

Class	Type		EP rang (%)	Mean EP (%)	Product number	Proportion	Sum
Pesticide category	Insecticides		35.59–98.88	60.54	n = 229	52.40%	100%
	Herbicides		35.40–83.38	53.91	n = 143	32.72%	
	Fungicides		35.54–95.43	50.86	n = 45	10.30%	
	Other pesticides		37.28–89.10	56.46	n = 20	4.58%	
Pesticide formulation	Emulsifiable concentrate		35.40–98.88	58.29	n = 365	83.52%	99.54%
	Micro-emulsion		36.11–68.29	47.52	n = 26	5.95%	
	Emulsion (oil in water)		35.86–63.03	42.42	n = 15	3.43%	
	Aqueous solution		35.59–87.83	63.13	n = 10	2.29%	
	Soluble concentrate		46.71–76.54	68.15	n = 7	1.60%	
	Suspension concentrate		36.40–84.90	55.38	n = 7	1.60%	
	Oil dispersion		43.58–64.05	51.17	n = 4	0.92%	
	Capsule suspension		/	35.54	n = 1	0.23%	
	Technical material[a]		49.10–59.58	54.34	n = 2	0.46%	0.46%
Active ingredient (Top 10)[b]	Top 1	Abamectin	35.64–89.10	54.36	n = 74	16.93%	71.85%
	Top 2	Chlorpyrifos	35.84–95.43	55.34	n = 37	8.47%	
	Top 3	Fluroxypyr	35.40–67.46	51.49	n = 23	5.26%	
	Top 4	Cyhalofop-butyl	38.20–80.79	54.25	n = 22	5.03%	
	Top 5	Beta-cypermethrin	36.75–94.09	69.38	n = 21	4.81%	
	Top 6	Acetamiprid	36.61–88.24	61.05	n = 19	4.35%	
	Top 7	Abamectin-aminomethyl	36.40–92.62	61.21	n = 15	3.43%	
		Quizalofop-P-ethyl	42.57–79.78	60.82	n = 15	3.43%	
	Top 8	Haloxyfop-P-methyl	46.72–62.99	53.19	n = 12	2.75%	
		Pyridaben	42.03–80.11	61.71	n = 12	2.75%	
		Clethodim	41.17–68.16	50.83	n = 12	2.75%	
	Top 9	Isoprothiolane	36.40–68.55	47.74	n = 11	2.52%	
		Triazophos	42.57–64.15	52.26	n = 11	2.52%	
	Top 10	Imidacloprid	35.71–85.52	70.20	n = 10	2.29%	
		Lambda-cyhalothrin	36.40–93.41	57.99	n = 10	2.29%	
		Prochloraz	35.54–64.73	48.63	n = 10	2.29%	

[a] They are scanty 2 solid samples in all of the pesticide products with high-VOC emission.
[b] There are too many active ingredients for the pesticide products with high-VOC emission, so here just listed Top 10 active ingredients occurred in single or mix component pesticide samples.

(CDPR, 2021; Wei, 2021).

3.3. VOC emission profiles of commercial pesticides in China

According to the amounts of commercial pesticides used in the 31 provinces of China in 2018 and the EP values of different pesticide formulations, the pesticide VOC emissions of the 31 provinces were estimated, the proportions contributed by different pesticide formulations were calculated, and the results are shown in Fig. 3 and Table S6. The pesticide VOC emissions of the 31 provinces demonstrated clear differences (Fig. 3a), and the highest province (Shandong) was 131 times higher than the lowest province (Tibet). In particular, the provinces with high-pesticide VOC emissions were Shandong (24.24 kt/y), followed by Hunan (21.30 kt/y) and Henan (21.20 kt/y). These provinces have extensive agricultural land and developed plantings. The provinces with the lowest emissions were Tibet, Qinghai, Tianjin, Ningxia, Beijing, and Shanghai (range 0.18–0.59 kt/y), which are metropolis or a northwest plateau with underdeveloped plantings. Emissions for the other 22 provinces ranged from 2.08 kt/y (Guizhou) to 19.28 kt/y (Hubei). In general, the pesticide VOC emissions were positively correlated with the amount pesticide used in each province (Table S6). The average emissions of pesticide VOCs from all provinces in China were 9.05 kt/y, with a calculated emission rate of VOC of 24.80 t/d, which was higher than the maximum (16.39 t/d for San Joaquin Valley) for five ozone nonattainment areas (NAAs) in California in 2019 (CDPR, 2019c).

The total VOC emission derived from commercial pesticides in China was 280 kt in 2018, among which 65.35% was contributed by EC, 9.55% by SC, 7.54% by EW, and <5% by the other nine formulations (Fig. 3b). This emission law was similar to the five ozone NAAs in California, where EC accounted for 27–49% (mean 41%) of non-fumigants in 2019, which was much higher than the other formulations (CDPR, 2019c). As EC contains benzene, toluene, xylene, and other volatile organic solvents, it is easy to volatilize more VOCs than other formulations (Guo et al., 2020; Liang et al., 2020; Toose et al., 2015). An obvious discrepancy was observed between the contribution proportion chart of the pesticide VOC emissions (Fig. 3b) and the amounts used (Fig. 1b) from different formulations, particularly for EC and WP. EC was responsible for using 26.75%, but contributed 65.35% of the VOC emissions, while WP was responsible for using 17.31%, but contributed 0.71% of the VOC emissions. These proportions suggest that the pesticide VOC emissions in China mainly came from liquid formulations, including EC, SC, and EW. Although applications of solid formulations (especially for WP) are very extensive, their VOC emissions account for a very small proportion. Therefore, transforming some liquid formulations into solid formulations would be an effective way to reduce pesticide VOC emissions.

The VOC emissions and proportions of different pesticide categories for all of China were estimated based on their amounts used in 2018 and the mean EP, including the EP guideline values from MEE (MEE, 2014) and the measured EP values from this study (Table S7). The mean EP of MEE was much higher than that in the present study, and the estimated VOC emissions from MEE were also much higher than those in this study, regardless of the category (herbicide, fungicide, or insecticide). The VOC emissions of these three categories estimated based on MEE data were 688 kt in 2018, which was 4.07 times that for all pesticides estimated by category in this study (269 kt, close to the value of 280 kt by formulations). Due to the larger number of samples and the detailed classification (12 formulations, Table S6), the estimate of VOC emissions from the present study is more accurate, while the VOC emissions derived from MEE data were over-estimated. Similarly, the proportion of VOC emissions contributed by the different pesticide categories might also be more accurate in the present study, as herbicides and insecticides contributed the most to VOC emissions, with proportions of 41.34% and 40.91%, respectively.

3.4. Environmental implications

To our knowledge, this is the first report on the use structure and VOC emissions of commercial pesticides in China based on a large-scale survey. The results demonstrate that a large quantity of VOCs is discharged during the production and use of commercial pesticides in China. This information provides some useful guidance for developing effective measures to reduce pesticide VOC emissions, and further diminish their contribution to O_3 and $PM_{2.5}$ formation. The most effective measure to reduce VOC emissions from pesticides is to further improve pesticide management policies (Craig et al., 2018; Yates et al., 2011). The Program of Zero Growth in Pesticides Use was enacted by the Chinese government in 2014. Subsequently, the use of pesticides in China has decreased obviously (Zhao et al., 2021); thus, this program should be carried out sequentially. At the same time, the Chinese government should formulate limit standards for high-VOC solvents during pesticide production, and strengthen supervision of solvent use in the pesticide industry. Some solid formulations with low-VOC emissions (such as WP, SP, and WG) should be produced preferentially, and low-VOC solvents should be substituted for high-VOC solvents during the production of liquid formulations (Guo et al., 2020; Purkait and Hazra, 2020). Finally, sufficient publicity should be initiated to guide farmers not to overuse pesticides, particularly pesticides with high-VOC emissions (e.g., top 10 active ingredients used as EC). For the provinces with the largest pesticide VOC emissions (including Shandong, Hunan, and Henan), it is more important to reduce the use of high-VOC pesticide

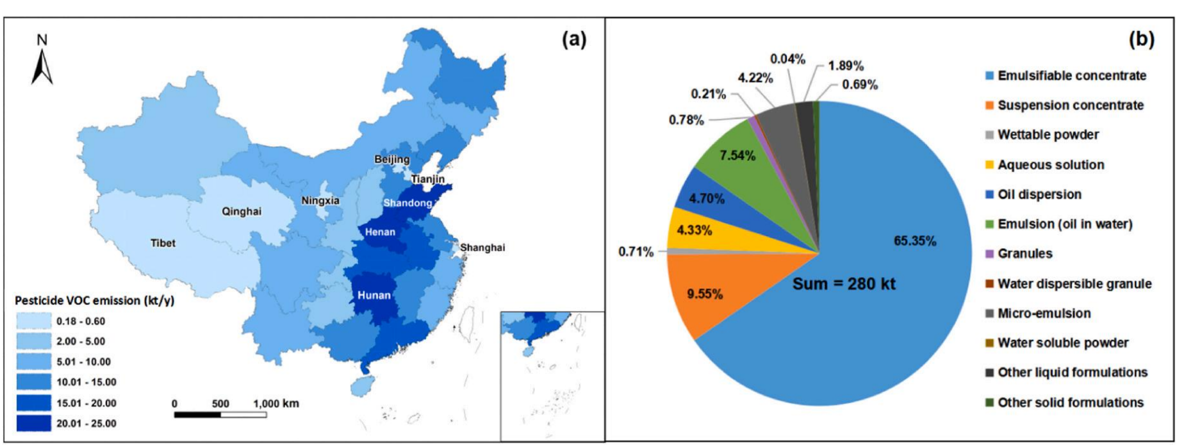

Fig. 3. VOC emission profiles for China's commercial pesticides in 2018. (a) Pesticide VOC emission for 31 provinces; (b) Total VOC emissions and their contributed proportions from different formulations.

products, and strengthen pest control through biological control technology rather than applying pesticides (Baker et al., 2020; Xu et al., 2017).

4. Conclusions

China is the largest consumer of pesticides in the world, and a massive amount of VOCs are released into the atmosphere during the production and application of commercial pesticides. Herbicides are more extensively applied than any other pesticide category in China, and the dominant formulations were EC, SC, and WP. The EP values of the pesticide VOCs for the liquid formulations were universally higher than those for the solid formulations. Among the selected high-VOC pesticide products, EC had the highest proportion (83.52%), and abamectin was the most prevalent active ingredient. About 280 kt of VOCs were emitted from commercial pesticides in China during 2018, among which EC was a prominent contributor, and Shandong, Hunan, and Henan were three provinces with the highest emissions. The emission rate of pesticide VOCs in China was 24.80 t/d, which is higher than in San Joaquin Valley, California. Perfecting pesticide management policy, strictly supervising pesticide production, and strengthening the publicity to reduce pesticide use are effective measures to diminish VOC emissions from pesticide applications.

Authorship contribution statements

De-Chun He: Conceptualization, Project administration, Funding acquisition, Resources, Original Draft Preparation, Validation, Review & Editing. **Fang-Hong Li:** Investigation, Sample collection and testing, Software, Verification. **Mian Wu:** Investigation, Sample collection and testing. **Hui-Li Luo:** Methodology, Investigation, Sample collection and testing. **Li-Qing Qiu:** Investigation, Visualization. **Xiao-Rui Ma:** Investigation, Supervision. **Jia-Wei Lu:** Methodology, Formal analysis, Data and material collection. **Wang-Rong Liu:** Methodology, Data analysis, Software, Visualization, Verification, Original Draft Preparation, Writing, Review & Editing. **Guang-Guo Ying:** Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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