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经济快速发展区场地污染特征、源-汇关系与管控对策专辑

我国经济快速发展区工业VOCs排放特征及管控对策

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# 我国经济快速发展区工业 VOCs 排放特征及管控对策

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**摘要:**近年来随着我国经济快速发展,挥发性有机物(VOCs)作为雾、霾和臭氧前驱物日益受到关注,经济快速发展区 VOCs 污染情况尤为复杂.本文对京津冀、长三角和珠三角的 12 种典型工业行业及垃圾、废水处理厂与综合工业园区、居民区的 VOCs 排放特征与分布趋势进行系统分析.解析出制药、橡胶和油漆喷涂为 12 种典型工业行业中 VOCs 平均排放浓度最高的 3 个行业,得到平均浓度分别为 541、499 和 450  $\text{mg}\cdot\text{m}^{-3}$ ,应给予高度关注.对比分析发现长三角与京津冀地区平均排放浓度最高是制药行业,分别为 112  $\text{mg}\cdot\text{m}^{-3}$  和  $1.00 \times 10^3 \text{mg}\cdot\text{m}^{-3}$ ;而珠三角地区油漆喷涂行业排放最高,平均浓度为  $1.04 \times 10^3 \text{mg}\cdot\text{m}^{-3}$ .进一步对 12 种典型工业行业 VOCs 种类分布情况进行分析,发现毒性大的芳香烃与卤代烃分别在油漆喷涂与制药行业中排放占比最高,达到 55.99% 和 26.57%.三大经济区中长三角地区居民区与综合工业园区附近 VOCs 浓度最低,京津冀地区浓度最高,与各地区工业排放分布情况一致.分析 2002~2018 年的数据发现居民区 VOCs 浓度整体呈现波动性下降趋势,尤其 2016 年后显著降低,反映出我国 VOCs 防治的相关政策、法律法规和标准及技术对现阶段 VOCs 控制起到了显著成效.

**关键词:**经济快速发展区;挥发性有机物(VOCs);工业行业;排放特征;分布趋势

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## Industrial Emission Characteristics and Control Countermeasures of VOCs in Chinese Rapid Economic Development Areas

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**Abstract:** With the rapid development of China's economy, volatile organic compounds (VOCs) as the precursor of smog and ozone are of increasing concern, especially in rapidly developing areas. This paper is a systematic analysis of VOCs emissions and distribution trends in 12 typical industrial sectors, garbage and wastewater treatment plants, comprehensive industrial parks, and residential districts in Beijing-Tianjin-Hebei, Yangtze River Delta, and Pearl River Delta Regions. The results show that pharmacy, rubber producing, as well as paint spraying are the top three industries among the 12 typical industries with the highest average VOCs emission concentrations at 541, 499, and 450  $\text{mg}\cdot\text{m}^{-3}$ , respectively. By comparison, the average emission concentration of VOCs from the pharmaceutical industry in Yangtze River Delta and Beijing-Tianjin-Hebei Region was, respectively, about 112 and  $1.00 \times 10^3 \text{mg}\cdot\text{m}^{-3}$ . The paint spraying industry in the Pearl River Delta region has the highest emission rate with an average concentration of  $1.04 \times 10^3 \text{mg}\cdot\text{m}^{-3}$ . The investigation pertaining to the distribution of different VOCs categories indicates that highly toxic aromatics and halogenated hydrocarbons account for the highest emissions in paint spraying and pharmaceutical industries, reaching ratios of 55.99% and 26.57%, respectively. Additionally, among the three major economic zones, the VOCs concentration is the lowest in residential areas and comprehensive industrial parks in the Yangtze River Delta but the highest in the Beijing-Tianjin-Hebei Region, which is consistent with the distribution of industrial emissions in each region. Moreover, the research reveals that VOCs concentration in residential districts experienced a fluctuating reduction from 2002 to 2018. The significant reduction since 2016 suggests that formulated policies, laws and standards, along with the performed techniques have made significant contributions to the control of VOCs.

**Key words:** rapid economic development regions; volatile organic compounds (VOCs); industrial sector; emission characteristics; distribution trend

随着我国经济的快速发展,工业的不断进步,大气污染问题也随之出现,其中我国经济快速发展区(长三角、珠三角和京津冀)地区接连发生雾、霾污染事件.文献[1]指出我国 500 个城市中仅不足 1% 的城市达到世界卫生组织推荐的空气质量标准.作为雾、霾的主要前驱体,挥发性有机物(volatile organic compounds, VOCs)的排放及危害备受关注.

VOCs 种类繁多,结构多样,文献[2]中将 VOCs 定义为:参与大气光化学反应的有机化合物,包括非甲

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烷烃类(烷烃、烯烃、炔烃、芳香烃等)、含氧有机物(醛、酮、醇、醚等)、含氮有机物、含硫有机物等,是形成细颗粒物和臭氧污染的重要前体物。同时 VOCs 对环境和人类的危害都极为严重,除雾、霾天气之外,还会导致臭氧(O<sub>3</sub>)、光化学烟雾和二次有机气溶胶(secondary organic aerosol, SOA)等污染天气,与此同时会导致人体呼吸困难和呼吸道感染等疾病的发生<sup>[3]</sup>。VOCs 的来源可以分为自然源及人为源<sup>[4]</sup>。在全球范围内,人为源排放的 VOCs 远少于自然源<sup>[5, 6]</sup>。然而在中国人为源和自然源的 VOCs 排放却处于同一水平<sup>[7, 8]</sup>。在区域尺度上,人为活动的 VOCs 排放量远远高于自然源的 VOCs 排放量<sup>[9, 10]</sup>。尤其是在高度城市化和工业化的经济快速发展区,人为源 VOCs 排放量是自然源的 3 倍<sup>[11]</sup>。

当前我国对污染防治工作越来越重视,文献[12]中明确指出全面落实打赢蓝天保卫战三年行动计划,加快重点行业 VOCs 排放治理,制定重点行业 VOCs 整治方案,并对经济快速发展区推进大气污染联防联控。VOCs 的污染防治与检测已成为大气治理的重点之一。目前我国对不同城市 VOCs 的排放研究较多<sup>[13-15]</sup>,但缺少对区域工业 VOCs 排放的整体分析,尤其是针对我国经济快速发展区 VOCs 的源排放结构和污染特征的系统研究。三大经济区是我国经济增长最快的 3 个区域,其中 2018 年,长三角、珠三角和京津冀地区生产总值为  $2.11 \times 10^5$ 、 $9.73 \times 10^4$  和  $8.51 \times 10^4$  亿元,分别占国内生产总值的 23.49%、10.80% 和 9.46%; 工业总产值分别占全国的 25.22%、12.32% 和 9.00%<sup>[16]</sup>。本文对我国近年来经济快速发展区不同工业排放 VOCs 的浓度与组成特征进行整理与分析,同时分析工业排放对综合工业园区和城市居民区周边大气的影响,结合我国 VOCs 防治的相关政策、法律法规和标准对现阶段 VOCs 控制现状进行了探讨。

## 1 材料与方法

### 1.1 研究区域

从 20 世纪 80 年代起,我国成为世界上经济增

长最快的国家之一。以长江三角洲、珠江三角洲和京津冀地区为代表的经济快速发展区是我国经济最具活力的区域,也是我国城市网络化发展最为迅速的区域。其中长三角地区的电子、油漆喷涂、农药和制药等行业占三大经济区的主导地位。珠三角地区较多的行业为皮革和印刷行业。而京津冀地区的炼油和钢铁焦化行业数量比其他地区明显较多<sup>[17]</sup>。本文选择长三角(包括上海、江苏、浙江和安徽)、珠三角(包括广东)和京津冀(包括北京、天津和河北)这三大经济区作为研究区。

### 1.2 研究对象

本文针对我国经济快速发展区人为源 VOCs 排放和污染特征进行系统分析,在工业源、生活源、农业源和移动源这 4 类人为源中,工业源排放占比最高。根据文献[18]中可得 2017 年我国大气中污染物的分布及 VOCs 的来源(图 1)。大气中 VOCs 的排放总量为 481.66 万 t, 占有所有废气的 17%。在 VOCs 的排放中,工业源 VOCs 排放量最高,占总排放量的 47%。工业源中,化学原料和化学制品制造业(如制药、农药、油漆和油墨行业等) VOCs 排放量最高,占 22%,石油、煤炭及其他燃料加工业(如炼油行业和钢铁焦化行业等)占 14%,橡胶和塑料制品业占 9%,其他行业(如食品加工行业、家具制造行业和电子产品等)占整体工业源排放的 55%。

我国经济快速发展区工业行业发展迅速, VOCs 排放高,对大气造成污染。图 2 反映了不同工业企业产生 VOCs 对居民区与工业园区的影响,工业 VOCs 污染源主要分为 VOCs 的生产、储存运输、VOCs 为原料的工艺过程、VOCs 产品使用和排放这 4 个过程<sup>[19]</sup>。在这些过程中产生的废气会对周边的城市居民区与工业园区附近的大气造成影响。

因此本文研究聚焦于 12 种典型工业行业(电子行业、家具制造、皮革行业、印刷行业、油漆喷涂行业、制药行业、橡胶行业、炼油行业、钢铁焦化行业、农药行业、食品加工行业及印染行业)及垃圾、废水处理厂与综合工业园区、居民区的 VOCs 相关数据。其中电子行业主要研制与生产电子设备与电子元

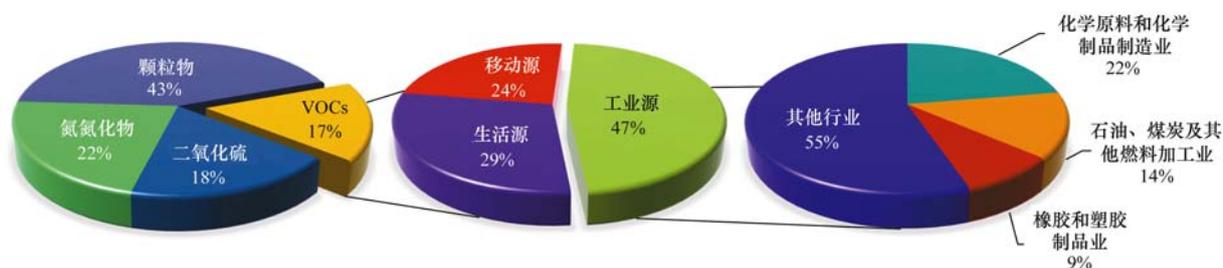


图 1 2017 年我国大气中污染物的分布及 VOCs 的来源分析

Fig. 1 Distribution of pollutants in the atmosphere and source analysis of VOCs in China in 2017

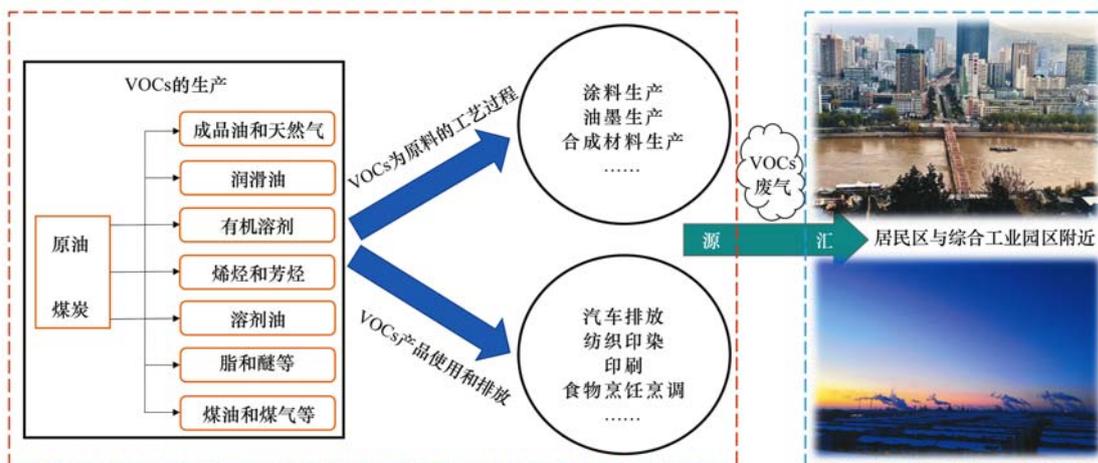


图 2 不同工业企业 VOCs 污染源对居民区和工业园区的影响示意

Fig. 2 Impact of VOCs pollution sources from different industrial enterprises on residential areas and industrial parks

件、仪器和仪表的工业,在电子元件刻蚀和电池的制备过程会产生 VOCs 的污染;家具制造业主要是使用木材、金属和塑料等材料,但是为了防止木材和金属等在长时间使用过程中发生腐蚀与氧化的情况,会在家具表面涂刷防腐剂、胶粘剂与其他涂料,此过程与风干过程都会散发出大量的 VOCs;皮革行业主要是以各类动物皮为原料进行加工处理,最终制得衣物和鞋包等产品,在加工过程中产生大量污染,给环境带来巨大压力与负担;印刷行业已初步形成以三大经济区为主的产业带,主要分为传统印刷与数码快印,油墨中含有大量有毒有害物质,在印刷时会挥发到大气中;油漆喷涂行业在对产品涂装与喷涂过程中会挥发出大量有机溶剂,不利于环境与人类健康;制药行业由原料药生产和药物生产两部分构成,由于包含化学合成、生物工程、发酵和提取这 4 大类合成方式,使得 VOCs 排放量较大;橡胶行业以天然及合成橡胶为原料生产各种橡胶制品,会使用大量苯系物,导致污染排放较高;炼油与钢铁焦化行业在炼制的过程中会让高分子化合物裂解为小分子化合物,从而挥发至大气中;农药行业与制药行业相类似,包含大量的苯、酚、醛和卤代烃类 VOCs;食品加工行业酿造过程(如酿醋和酿酒等)中微生物会合成有机物,由此导致食品加工行业会产生 VOCs;印染行业的染料多数为有机合成染料,在上染过程中部分染料由于其挥发性,导致印染行业的 VOCs 排放量升高。

### 1.3 样点位置概况及数据分析

12 种典型工业行业的采样点主要位于各生产线、车间厂房与废气排放烟囱,数据量共 165 个;垃圾处理厂与污水处理厂分别采样于堆肥、焚烧车间和曝气、发酵车间,数据量共 28 个;居民区采样点主要包括城市中以集中住宅区域、商业区域、交通繁

忙区域和学校等无主要工业园区的区域,数据量共 143 个;综合工业园区附近主要选取典型工业园区附近的家属区或空地作为研究场所,数据量共 42 个。基于 Meta 分析方法对所收集的数据进行质量评价与统计分析,探讨三大经济区中 12 种典型工业行业及垃圾、废水处理厂 VOCs 排放情况及对综合工业园区、居民区的影响。Meta 分析实质上是汇总相同研究目的的多个研究结果,通过异质性检验,分析评价其合并效应量的一系列过程,相较于传统统计方法,其结果更为系统和全面,可以最大限度减少偏倚,确保科学、客观和真实性<sup>[20-22]</sup>。

## 2 结果与讨论

### 2.1 不同行业企业大气中 VOCs 污染特征

本文调查了“十三五”期间规划纲要中所提及的 VOCs 重点排放行业中的 12 种典型工业行业<sup>[23-61]</sup>,同时对垃圾处理厂<sup>[34,62-65]</sup>和污水处理厂<sup>[66,67]</sup>也进行了简要分析。表 1 与图 3 的数据可看出,制药行业、橡胶行业和油漆喷涂行业 VOCs 的平均排放浓度较高,分别为 541、499 和 450  $\text{mg}\cdot\text{m}^{-3}$ ,而钢铁焦化、农药行业、食品加工和印染行业 VOCs 排放较低。由于中位数能够反映出一个行业的整体情况,消除了离散值对整体的影响,所以对各行业的中位数进行比较发现橡胶行业、制药行业和印刷行业 VOCs 中位数较高,分别为 197、97.2 和 22.6  $\text{mg}\cdot\text{m}^{-3}$ 。与文献[14]相比,橡胶行业及塑料制品业虽然只占工业中 VOCs 排放总量的 9%,但是橡胶行业排放浓度高,所以需要对其进行一定的监管与调控。油漆喷涂、制药和炼油厂的离散点较高,主要原因是部分采样点处于特殊工段,如油漆喷涂的喷漆车间、制药厂的发酵车间和炼油厂的蒸馏车间, VOCs 浓度相对较高。

表 1 12 种典型工业行业及垃圾、废水处理厂 VOCs 排放情况/ $\text{mg}\cdot\text{m}^{-3}$

Table 1 VOCs emissions from 12 typical industries and garbage and wastewater treatment plants/ $\text{mg}\cdot\text{m}^{-3}$

行业	经济快速发展区			长三角			珠三角			京津冀		
	范围	平均浓度	中值	范围	平均浓度	中值	范围	平均浓度	中值	范围	平均浓度	中值
电子行业	0.17~132	21.9	3.02	1.25~4.08	10.4	3.02	0.17~0.23	0.19	0.18	21.7~132	76.7	76.7
家具制造	2.36~182	44.6	20.3	—	—	—	2.36~182	44.6	20.3	—	—	—
皮革行业	0.11~15.3	6.27	1.98	—	—	—	0.11~15.3	6.27	1.98	—	—	—
印刷行业	8.39~96.9	31.1	22.6	—	—	—	8.39~96.9	31.1	22.6	—	—	—
油漆喷涂	$0.74\sim 3.03\times 10^3$	450	12.8	$0.74\sim 73.4$	12.2	5.20	$2.99\sim 3.03\times 10^3$	$1.04\times 10^3$	784	$4.04\sim 115$	41.6	5.52
制药行业	$4.16\times 10^{-2}\sim 5.42\times 10^3$	541	97.2	$9.01\sim 309$	112	97.2	—	—	—	$4.16\times 10^{-2}\sim 5.42\times 10^3$	$1.00\times 10^3$	109
橡胶行业	$0.30\sim 1.57\times 10^3$	499	197	—	—	—	—	—	—	$0.30\sim 1.57\times 10^3$	49.9	197
炼油行业	$0.21\sim 1.23\times 10^3$	114	9.81	$0.21\sim 11.2$	3.01	2.57	$241\sim 1.23\times 10^3$	584	277	$9.81\sim 225$	87.6	53.9
钢铁焦化	$2.67\times 10^{-2}\sim 1.29$	0.38	0.11	0.18	0.18	0.18	—	—	—	$2.67\times 10^{-2}\sim 1.29$	0.45	$4.38\times 10^{-2}$
农药行业	8.99~10.7	10.0	10.4	—	—	—	—	—	—	8.99~10.7	10.0	10.4
食品加工	0.18~0.97	0.50	0.31	0.18~0.97	0.50	0.31	—	—	—	—	—	—
印染行业	0.76~12.6	5.00	3.05	1.68~12.6	6.23	5.15	—	—	—	0.76~3.05	1.90	1.90
垃圾处理	0.37~470	83.0	15.5	—	—	—	—	—	—	—	—	—
废水处理	0.58~2.60	1.35	1.12	—	—	—	—	—	—	—	—	—

1) “—”表示未进行数据汇总

各地区排放最高的行业分别是长三角地区的制药行业、珠三角地区的油漆喷涂行业和京津冀的制药行业,平均浓度分别为 112、 $1.04\times 10^3$  和  $1.00\times 10^3\text{ mg}\cdot\text{m}^{-3}$ . 最大值为 309、 $3.03\times 10^3$  和  $5.42\times 10^3\text{ mg}\cdot\text{m}^{-3}$ . 从中位数来看京津冀地区的橡胶行业则高于制药行业,长三角制药行业、珠三角油漆喷涂行业和京津冀橡胶行业 VOCs 中位数分别为 97.2、784

和  $197\text{ mg}\cdot\text{m}^{-3}$ . 制药行业中主要分为发酵类、提取类、化学合成类与生物工程类 4 种,其中发酵类 VOCs 贡献量最高,而生物工程类 VOCs 贡献最低<sup>[45, 48]</sup>. 长三角地区中制药行业种类较为全面,同时长三角地区的废气处理设备多采用较为先进的蓄热式催化燃烧工艺与等离子体催化氧化处理技术等,使得 VOCs 排放降低. 而报道中京津冀地区的制

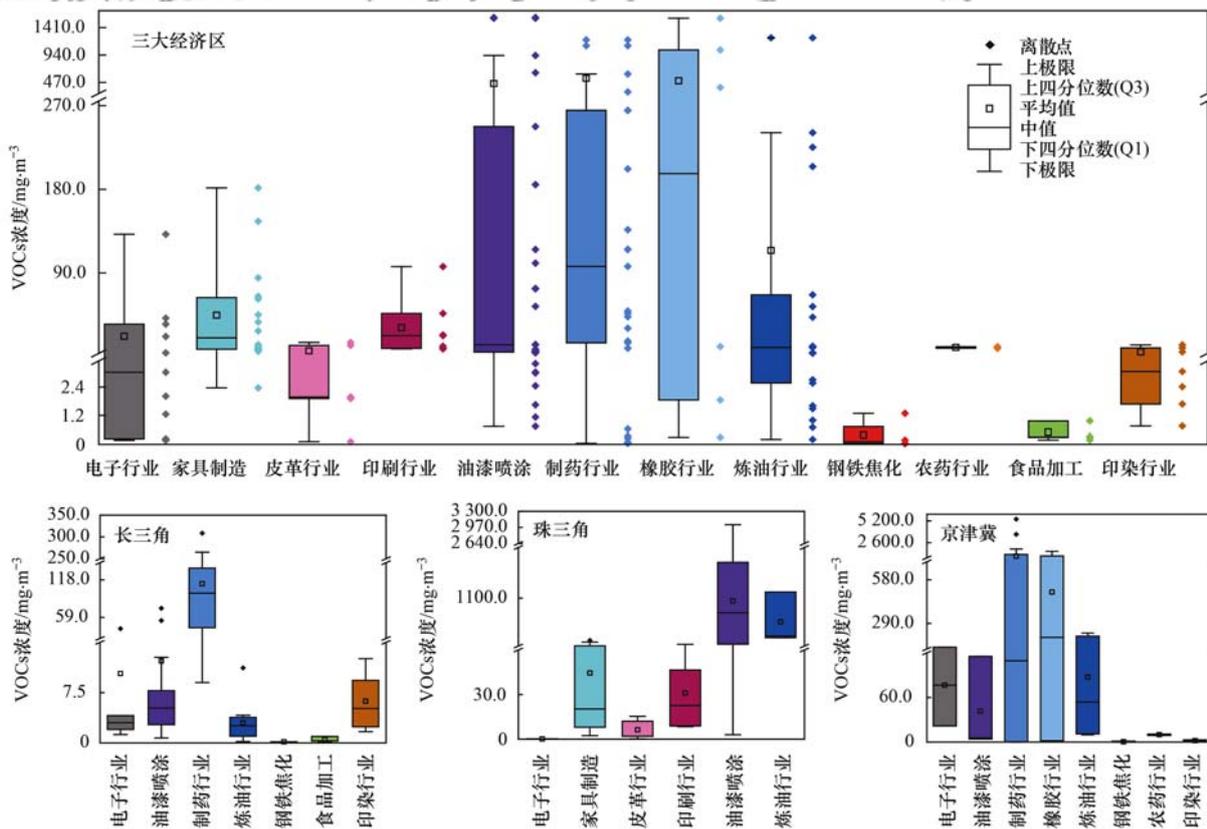


图 3 研究区域 12 种典型行业 VOCs 排放情况

Fig. 3 VOCs emissions of 12 typical industries in the research area

药行业则多以发酵类为主. 由此导致长三角地区 VOCs 排放量远低于京津冀地区. 珠三角地区油漆喷涂行业远高于其他两个地区, 其中珠三角油漆喷涂行业 VOCs 排放范围为  $2.99 \sim 3.03 \times 10^3 \text{ mg} \cdot \text{m}^{-3}$ , 而长三角与京津冀 VOCs 排放浓度范围分别为  $0.74 \sim 73.4 \text{ mg} \cdot \text{m}^{-3}$  和  $4.04 \sim 115 \text{ mg} \cdot \text{m}^{-3}$ . 珠三角企业规模较大, 包括大型金属表面喷涂、船舶喷涂、塑料表面喷涂等众多行业, 而长三角与京津冀主要以汽车零部件、整车喷涂和其他较为小型工件为主, 因此导致珠三角地区油漆喷涂行业 VOCs 排放较高.

根据报道珠三角地区未发现制药与印染行业的相关研究, 可能是这两类行业分布少、规模小等原因. 长三角印染行业 VOCs 平均浓度为  $6.23 \text{ mg} \cdot \text{m}^{-3}$ , 排放比京津冀地区高, 其主要贡献省份为纺织品产量名列前茅的浙江省<sup>[61]</sup>. 而珠三角地区与其他地区相比特有的行业为家具制造、皮革与印刷行业, 其平均排放浓度分别为  $44.6$ 、 $6.27$  和  $31.1 \text{ mg} \cdot \text{m}^{-3}$ , 浓度范围为  $2.36 \sim 182$ 、 $0.11 \sim 15.3$  和  $8.39 \sim 96.9 \text{ mg} \cdot \text{m}^{-3}$ , 整体排放较低. 从 3 个区域不同行业浓度分布来看, 京津冀地区 VOCs 排放较大, 整体污染程度也较为严重; 相比较而言长三角地区 VOCs 排放较低, 污染程度也随之降低.

VOCs 中芳香烃和卤代烃较其他烃类的毒性更高, 同时芳香烃与卤代烃的降解过程较为困难, 对生态环境和人类健康造成了极大影响, 由此本文对各行业的芳香烃与卤代烃排放进行了统计, 图 4 为不同行业芳香烃与卤代烃排放占比, 可以看出 12 种典型工业行业中芳香烃排放占比较高的分别是油漆喷涂、皮革和橡胶行业, 占比分别为  $55.99\%$ 、 $50.88\%$

和  $50.32\%$ . 油漆喷涂行业大量使用以有机溶剂为分散介质的溶剂型涂料, 包括苯、甲苯和二甲苯等多种芳香烃类物质; 有机溶剂作为稀释剂与添加剂在皮革行业也被广泛使用, 同时包含芳香烃的防霉剂、染料和加脂剂等因疏水性易被皮革纤维吸附, 导致芳香烃在皮革行业中占比较大. 橡胶行业中为防止橡胶老化多会喷涂清漆等有机涂料加以保护, 使得炼胶车间和喷涂车间芳香烃浓度很高. 而农药行业和食品加工行业排放占比都小于  $10\%$ . 卤代烃排放占比前三的行业分别是制药行业、电子行业和钢铁焦化行业, 占比分别为  $26.57\%$ 、 $16.05\%$  和  $14.05\%$ , 药类制品中包含的卤族元素可以延长药物作用时间, 增强药效作用, 因此在生产制造的过程中会排放过多的卤代烃. 电子产品中一些半导体的刻蚀技术车间会释放卤代烃. 钢铁焦化行业中多环芳烃在高温条件下与含氮、氧和硫等杂环芳烃燃烧反应中, 其降解产物与氯自由基发生了强烈反应<sup>[57]</sup>, 导致卤代烃的生成. 排放占比较低的行业有橡胶行业、印染行业和皮革行业, 其排放占比都小于  $5\%$ . 除制药和农药行业卤代烃含量超过芳香烃之外, 其它 10 个行业芳香烃的排放均高于卤代烃.

目前垃圾处理厂与污水处理厂排放的 VOCs 浓度也相对较高, 相关部门开始逐渐关注垃圾和污水处理厂的废气排放情况, 但由于当前对其研究与数据的量较少, 所以本文对三大经济区垃圾和污水处理厂的 VOCs 排放情况只进行了简要探讨. 垃圾处理厂除了处理生活垃圾外, 还会对工厂所产生的有害垃圾进行更进一步的处理. 本文调查的垃圾处理厂对生活垃圾和食品加工行业和固体塑料垃圾进行相应的处理. 由于大量的堆肥与焚烧, 导致处理车间

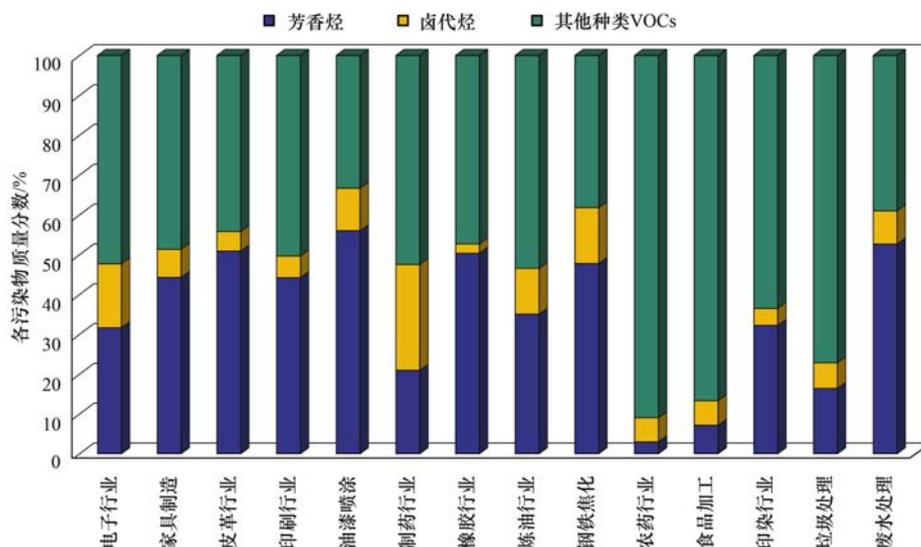


图 4 不同行业芳香烃与卤代烃排放占比

Fig. 4 Emission ratios of aromatic hydrocarbons and halogenated hydrocarbons in different industries

VOCs 排放量巨大,垃圾处理厂的 VOCs 平均浓度为  $83.0 \text{ mg}\cdot\text{m}^{-3}$ , 高于皮革、钢铁、食品与印染行业 VOCs 平均浓度. 其中芳香烃占比 16.4%, 卤代烃占比为 6.42%<sup>[34,62~65]</sup>. 由于大部分企业废水必须达到排放标准才可以进行排放,所以污水处理厂处理的主要为城市生活废水,在化粪池和对污泥进行曝气、堆肥和发酵时会产生 VOCs, 平均浓度为  $1.35 \text{ mg}\cdot\text{m}^{-3}$ , 相对于其他行业较低,其中芳香烃占比为 52.66%, 卤代烃占比为 8.33%<sup>[66,67]</sup>. 整体上,农药、食品加工和垃圾处理的其他种类 VOCs 排放相对来说较高,其主要的种类为烷烃和烯烃,部分含有少量炔烃、醛和醚等 VOCs.

## 2.2 居民区和综合工业园区附近大气中 VOCs 污染特征

三大经济快速发展区居民区<sup>[13~15,23,68~142]</sup>与综合工业园区附近<sup>[13,15,65,69,73,107,113,114,118,121,124,143~169]</sup>

VOCs 的浓度数据统计如图 5. 可以看出三大经济区长三角、珠三角和京津冀的居民区 VOCs 平均浓度分别为  $8.96 \times 10^{-2}$ 、0.13 和  $0.15 \text{ mg}\cdot\text{m}^{-3}$ , 中值为  $7.83 \times 10^{-2}$ 、0.12 和  $0.10 \text{ mg}\cdot\text{m}^{-3}$ , 浓度范围为  $1.56 \times 10^{-2} \sim 0.24$ 、 $3.20 \times 10^{-2} \sim 0.29$  和  $1.20 \times 10^{-2} \sim 0.50 \text{ mg}\cdot\text{m}^{-3}$ . 京津冀地区最高点浓度为  $0.50 \text{ mg}\cdot\text{m}^{-3}$ , 此数据采自 2013~2014 年石家庄地区, 由于冬季供暖等诸多原因导致雾、霾天气, 进而使得采样点浓度较高. 长三角、珠三角和京津冀地区综合工业园区附近的 VOCs 平均浓度分别为 0.18、0.27 和  $0.62 \text{ mg}\cdot\text{m}^{-3}$ , 中值为  $7.42 \times 10^{-2}$ 、 $7.76 \times 10^{-2}$  和  $0.37 \text{ mg}\cdot\text{m}^{-3}$ , 浓度范围为  $2.16 \times 10^{-2} \sim 1.74$ 、 $0.36 \times 10^{-2} \sim 0.93$  和  $3.23 \times 10^{-2} \sim 2.04 \text{ mg}\cdot\text{m}^{-3}$ . 长三角与珠三角平均浓度远高于中值浓度, 反映出这两个地区大部分企业对尾气处理较为完善, 但部分企业排放仍然存在不达标的情况, 需企业与相关部门进行排查与改善. 长三角地区最高点浓度为  $1.74 \text{ mg}\cdot\text{m}^{-3}$ , 此点在 2016 年常州市某旧农药企业搬迁后场主导风向下游地区进行采样, 由于企业设备老旧且尾气处理设施不完善, 导致采样点的数值偏高. 整体分析发现综合工业园区附近的 VOCs 浓度越高, 居民区的 VOCs 浓度也会相应地变高. 结合图 3 和图 5 来看, 长三角地区的各行业总体排放情况较低, 综合工业园区附近的 VOCs 浓度范围最小, 中值最小; 而京津冀地区 VOCs 排放较高的企业比较多, 综合工业园区附近 VOCs 浓度范围最大, 中值最高. 说明了综合工业园区附近的 VOCs 平均浓度受到各行业 VOCs 排放的影响, 反映出了长三角地区排放的废气处理较好, 大部分原因是因为长三角地区相对发展较为迅速, 处理设施与工艺

较为先进. 而京津冀地区近几年雾、霾天气频发, 部分原因是工业园区设施比较陈旧, 管理制度与长三角地区相比不够规范, 相关规定不够完善<sup>[88,97,113,146]</sup>.

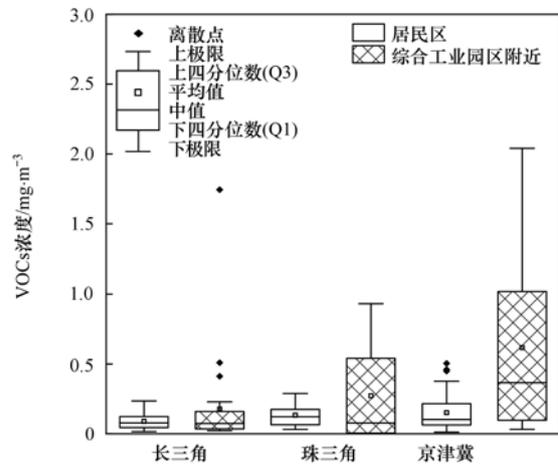


图 5 三大经济区居民区与综合工业园区附近 VOCs 浓度

Fig. 5 VOCs concentration near residential areas and comprehensive industrial parks of three economic zones

由于居民区可以反映出 VOCs 整体管控情况, 所以对各年份的居民区 VOCs 的排放浓度进行分析 (图 6). 2016 年“十三五”规划出台后 VOCs 浓度呈现明显下降趋势, 说明近些年来相关部门对我国 VOCs 治理管控取得了显著成效.

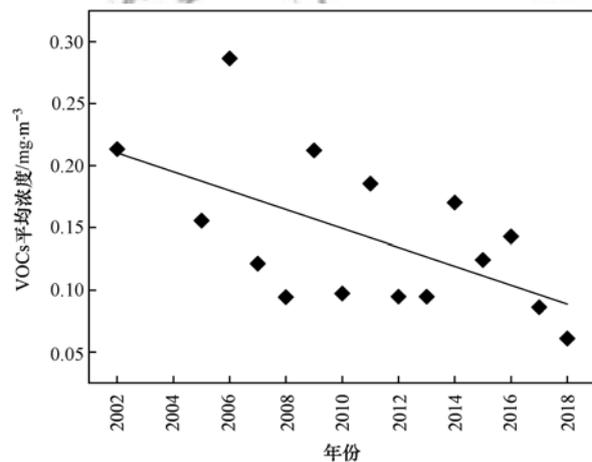


图 6 居民区 VOCs 年度变化

Fig. 6 Annual VOCs variation in residential areas

## 2.3 VOCs 管控现状与问题分析

我国对 VOCs 重视始于“十一五”末端,“十二五”期间逐渐出台各项相关法律法规、技术政策和排放标准, 但是体系依旧不够完善, 政策法规相对较为滞后, 多数污染防治技术基于末端治理技术, 典型行业最佳可行控制技术尚未形成 (图 7). 文献 [170] 中提出要强化源头防控, 深化质量管理, 实行全程管控, 加大保护力度并加快制度创新. 其中强化源头防控起主导地位, 包括加强重点开发区管理治

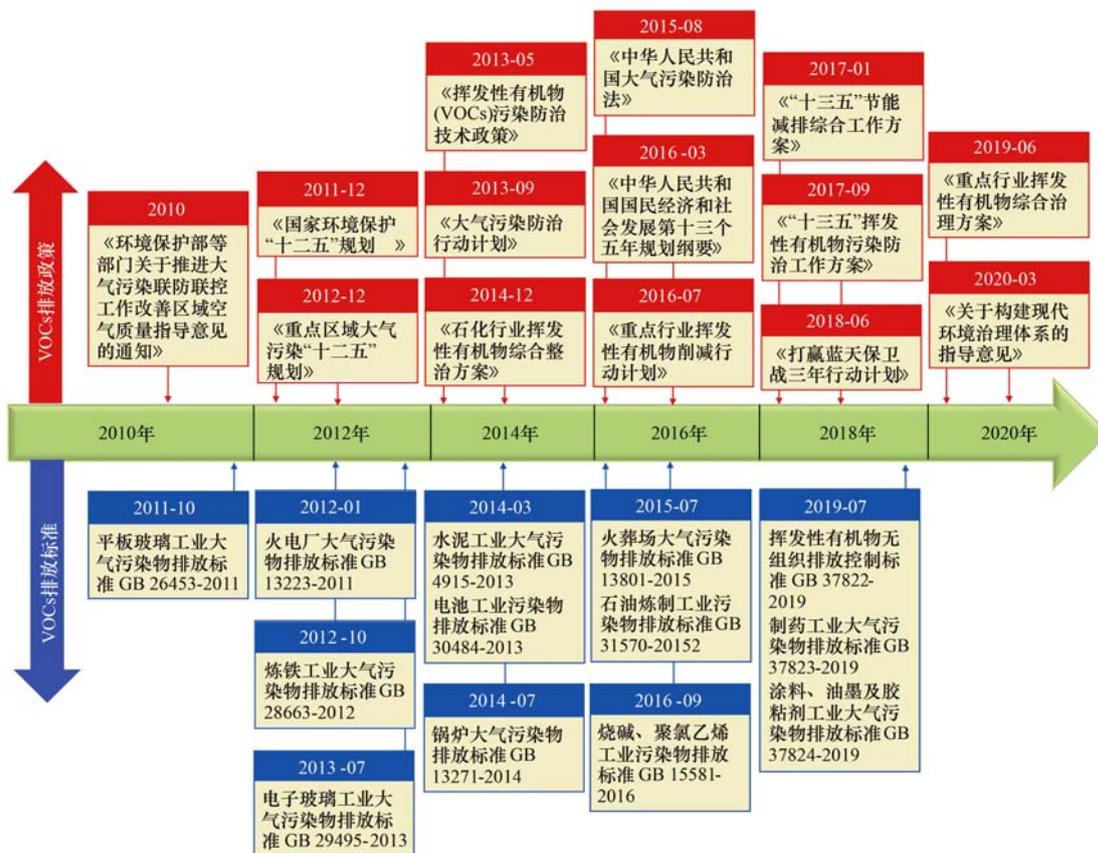


图7 我国 VOCs 污染治理制定的政策和标准

Fig. 7 Policies and standards on VOCs pollution control in China

理,减少工业化和城镇化对生态的影响. 文献[18]中指出本次普查对部分行业和领域 VOCs 进行了尝试性调查,排放量1 017.45万 t.

2010年我国首次从国家层面提出将 VOCs 列为大气污染联防联控的重点污染物之一,开启了我国 VOCs 管控与治理之路. 在“十二五”规划中加强挥发性有机物的控制过程,首次明确了要大力降低 VOCs 的排放,同时针对重点区域与行业展开治理,构建并完善 VOCs 污染防治体系<sup>[171]</sup>. 2013年针对我国大气污染形势严峻及雾、霾等各项问题,文献[172]中提出全面推行清洁生产,钢铁、化工和冶炼等行业采用先进技术、工艺和设备,推进非有机溶剂型涂料与农药等产品,并对重点行业 VOCs 的排放纳入污染费征收范围,再次强调对 VOCs 排放量进行控制. 同时针对我国经济快速发展区提出至2015年底完成燃煤电厂、锅炉等行业治理设施建设和改造与石化企业 VOCs 综合治理. 文献[173]中首次明确将 VOCs 作为区域大气污染联合防治的大气污染物之一. 此次修改对于保障公众健康、推进生态文明建设、解决重点污染问题和促进经济社会可持续发展具有重要意义. “十三五”期间规划纲要强调大力推进污染物达标排放和总量减排,明确提出在重点区域、重点行业推进挥发性有机物排放总量控制,全

国排放总量下降超过10%,提出加快石油炼制与石油化工、涂料、油墨、农药、汽车、印刷、橡胶制品、合成革、家具和制鞋等重点行业 VOCs 削减,明确实施原料替代工程、工艺技术改造工程、回收及综合治理工程等任务<sup>[174]</sup>. 文献[175]中将 VOCs 归入减排目标,并提出到2020年 VOCs 排放总量比2015年下降10%以上. 文献[176]指出,到2025年,建立健全环境治理的各项相关体系,落实各类主体责任,提高市场主体和公众参与的积极性,形成多元化治理体系结构. 总体上看我国 VOCs 整体排放呈现先增长后下降的趋势,2011年人为源排放量为2 297.65万 t,2017年增长至2 543.41万 t,2018年首次出现下降,2019年排放量为2 342.41万 t<sup>[177]</sup>.

文献[2]明确指出强化长三角、珠三角和京津冀地区 VOCs 减排,同时各地区也逐渐形成较为完整的政策与治理方案. 长三角三省一市政府2019年颁布文献[178]; 广东省2018年发布文献[179]; 京津冀地区一省两市也首次制定统一 VOCs 排放标准,颁布文献[180],以降低部分行业的 VOCs 排放. 各省市也相应出台应对本省污染情况的对策与防治规划.

文献[12]中第八条指出我国对油漆喷涂、石化炼油和包装印刷等重点行业相关标准已经明确,结

合本文可知此类行业排放较高,需要加强管控,合理排放.但部分行业如橡胶、家具制造与皮革行业等 VOCs 排放较高却暂未出台相关标准,上述文件中第六条明确指出要加快制定此类重点行业排放标准,加强管控力度,合理生产,稳步发展.文献[181]修订发布后,VOCs 控制思路逐步走向了全过程控制技术体系的构建.该体系分为源头控制、过程控制与末端治理技术 3 大类.

源头控制中首要大力推行环保型材料的使用,尤其是在涂料、油墨和胶粘剂的使用方面,寻找合适且无毒无害的替代物是首要任务.“十二五”规划到“十三五”规划期间,源头替代在不断改进,主要集中在水性涂料替代油性涂料,覆盖于汽车和船舶等交通设备的制造、木制家具制造企业、钢材等众多工业装涂与包装印刷行业等.文献[2]提出了除水性涂料或者油墨之外,高固体组分、粉末涂料等环保型涂料也进行大力推广.如近十年我国油漆喷涂行业中乘用车的水性涂料使用率从 14% 发展到 83%<sup>[177]</sup>.

过程控制主要原则在于密闭化,从生产的过程中解决排放问题.但由于部分工业无法实现密闭,所以也可以采用局部收集的方式.文献[182]明确梳理了 5 类无法实现密闭典型源(物料储存、物料转移和输送、工艺过程、设备与管线组件泄漏、敞开液面控制),并且提出实施分类管理、强调控制过程、采取先进工业设备与技术和规定去除率最低限制等要求,有效地降低了 VOCs 的排放.

末端治理技术主要包括两大类,即氧化分解技术与回收技术.氧化分解技术包括催化氧化、热氧化、光氧化与生物降解技术等.热氧化分解处理效率最高,77.3%~98.0% 不等,在油漆喷涂和印刷行业等都取得了不错的成效<sup>[183]</sup>.回收技术则主要以物理方面的冷凝、膜分离与吸收吸附技术为主.从使用 TSR 系列回收技术处理工艺的上海某造漆厂检测来看,处理效率达 87.5%<sup>[183]</sup>.VOCs 末端治理技术的选择比较复杂,除了需要考虑风量、浓度、物种的特征外,还需要考虑废气排放的波动性和连续性<sup>[184-188]</sup>.从全国角度出发,相对落后的城市对 VOCs 的治理较晚,且在治理方面实际效果也参差不齐.因此基于行业和 VOCs 物种开展有效性评价<sup>[184,189]</sup>,同时考虑处理效果、技术经济评估和综合效益评价等因素<sup>[190,191]</sup>,需建立比较综合且全面地评价方法来指导企业和政府选择适用的 VOCs 末端治理技术.

目前治理 VOCs 存在的问题依旧较多.油漆喷涂、印染和印刷等行业源头控制力度较差,同时由于成本、政策等原因,导致有机溶剂等低 VOCs 含量原辅材料使用率很低.制药行业卤族元素大量使用,橡

胶和家具等行业中芳香烃使用较多,导致无组织排放问题突出.VOCs 产排污环节较多,无组织排放特征明显,众多企业暂未采取有效治理手段.农药和食品行业由于废气排放少,治污设施不被重视,通常简易低效.且 VOCs 成分复杂,治理技术多样,部分行业监管能力不足,导致无法达到预期的治理效果.

### 3 结论

本文对 3 个经济快速发展区 12 种典型工业行业 VOCs 整体排放情况进行探究,可以看出排放最高的 3 个行业是制药、橡胶和油漆喷涂,其平均排放浓度分别为 541、499 和 450  $\text{mg}\cdot\text{m}^{-3}$ .进一步识别出长三角、珠三角和京津冀各地区平均排放浓度最高的行业分别为制药行业、油漆喷涂行业和制药行业,平均浓度分别为 112、 $1.04 \times 10^3$  和  $1.00 \times 10^3$   $\text{mg}\cdot\text{m}^{-3}$ .芳香烃与卤代烃在 VOCs 中毒性与危害较高,由此本文探究 12 种典型工业行业中芳香烃与卤代烃排放占比.油漆喷涂行业的芳香烃排放占比最高,占总 VOCs 排放的 55.99%,卤代烃占比最高的行业为制药行业,占其 VOCs 排放量的 26.57%.与 12 种典型工业行业相比,三大经济区中垃圾处理厂和污水处理厂的 VOCs 平均浓度为 83.0  $\text{mg}\cdot\text{m}^{-3}$  和 1.35  $\text{mg}\cdot\text{m}^{-3}$ ,垃圾处理厂排放高主要由于大量的堆肥与焚烧,排放量高于皮革、钢铁、食品与印染行业 VOCs 平均浓度,需要得到相关部门的重视.居民区与综合工业园区附近的 VOCs 排放浓度最高的区域为京津冀地区,浓度分别为 0.15  $\text{mg}\cdot\text{m}^{-3}$  和 0.62  $\text{mg}\cdot\text{m}^{-3}$ ,京津冀地区雾、霾天气需要持续关注.由居民区逐年变化可发现 VOCs 呈现整体下降的趋势,表明我国相关政策的出台与法律法规的颁布使 VOCs 的排放情况显著下降,相关标准也在逐一健全,VOCs 控制思路开始稳步构建,制药、橡胶和油漆喷涂等排放严重行业中各项治理技术虽存在部分问题,但目前正在逐步完善.

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