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地级市域工业 VOCs 排放源产排特性及其控制技术应用现状：以秦皇岛市为例

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摘要: 对秦皇岛市 609 家工业企业 VOCs 的源排放和污染控制技术做了调研。结果表明, VOCs 排放源排放的气体流量以石油加工、炼焦和核燃料加工业最高 ($>10^5 \text{ m}^3 \cdot \text{h}^{-1}$)。其余行业主要集中在 $10^3 \sim 10^5 \text{ m}^3 \cdot \text{h}^{-1}$ 之间。各行业源排放的 VOCs 浓度均小于 $1\,000 \text{ mg} \cdot \text{m}^{-3}$, 各行业的 VOCs 排放速率差异性较大, 介于 $50 \sim 10\,000 \text{ g} \cdot \text{h}^{-1}$ 之间。其中交通运输设备制造业、石油加工、炼焦和核燃料加工业、机械设备制造业、印刷和记录媒介复制业及化学原料和化学制品制造业的排放浓度和排放速率均较高。和国内之前的调查研究相比, 秦皇岛市工业企业 VOCs 的排放水平相对较低。此次调研的 609 家工业企业中拥有 VOCs 处理设施的案例共 109 个。吸附技术应用的占比最大 (69%)。其次为吸收技术 (19%)。

关键词: 挥发性有机物 (VOCs); 排放分析; 治理技术; 应用现状; 秦皇岛

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Characteristics of Industrial VOCs Emission Sources and Control Technology Application in a Prefecture-level City Region-Based on Qinhuangdao City

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Abstract: Volatile organic compound (VOCs) emissions and control technologies of about 609 industrial enterprises in Qinhuangdao City were investigated in this study. The results showed that the exhausted emission flow rates from the industries of oil processing, coking, and nuclear fuel processing were found to be the largest sources of VOCs in Qinhuangdao City (normally above $10^5 \text{ m}^3 \cdot \text{h}^{-1}$), whereas the other industrial emission flow rates were mainly within the range of $10^3 \sim 10^5 \text{ m}^3 \cdot \text{h}^{-1}$. The detected VOC concentrations for all the industries were less than $1\,000 \text{ mg} \cdot \text{m}^{-3}$. The VOCs emission rates were between $50 \sim 10\,000 \text{ g} \cdot \text{h}^{-1}$, but demonstrated different characteristics among the various industries. It was found that the industries of transportation equipment manufacturing, petroleum processing, coking, nuclear fuel processing, machinery and equipment manufacturing, printing and reproduction of recorded media, and chemical raw material and chemical product manufacturing had much higher concentrations and emission rates than other industries did. However, the overall VOCs emission level from this city was still lower when compared to previous reports for other regions of China. The investigation of the VOCs control technology application showed that there were 109 constructed or operated VOCs treatment facilities among the 609 industrial enterprises. Activated carbon adsorption technology accounted for the largest proportion among the various techniques, with 69%, followed by absorption technology (19%).

Key words: volatile organic compounds (VOCs); emission analysis; treatment techniques; application status; Qinhuangdao City

随着我国工业化和城市化的发展,大气污染问题日益严重^[1,2]。挥发性有机物 (volatile organic compounds, VOCs), 不仅能造成严重的环境污染, 形成光化学烟雾现象和雾、霾天气, 同时还会造成臭氧污染^[3~6]。VOCs 对人体健康同样有着极大的威胁, 使人们产生不适的反应, 有些 VOCs 还具有较强的致癌性^[7~10]。

“十三五”规划明确指出, 要控制重点地区重点行业 VOCs 排放, 保证全国总排放量下降 10%^[11]。城市群是我国城市化和工业化的核心区域, 面临着更大的环境压力^[12]。工业源 VOCs 排放不仅种类多, 排放比重也很高^[13]。对于京津冀、长三角、珠三角、长江中游和成渝城市群的重点行业 VOCs 排

放特征的研究已有相关报道^[14~20]。

中小型地级市作为城市群的组成部分, 对经济发展同样起着至关重要的作用。然而对于地级市域工业 VOCs 排放源产排特性的研究还十分欠缺。因此, 本文以秦皇岛市作为调研对象, 对其主要工业 VOCs 排放源进行了调研, 对不同工业行业的 VOCs 排放进行了分析, 并分析了不同 VOCs 控制技术的应用和运行情况等, 以期为秦皇岛市 VOCs 减排潜力预算和处理技术选择提供一定的参考依据。

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1 材料与方法

1.1 行业分类方法

根据《国民经济行业分类》(GB/T 4754-2011)中关于对 VOCs 排放重点行业的划分方法,并与秦皇岛市实地情况相结合,对秦皇岛市所涉及 VOCs 的工业行业划分为 15 类(如图 1)。

1.2 调研内容与检测方法

调研范围涉及秦皇岛市海港区、经济技术开发区、山海关区、北戴河区、抚宁县、昌黎县、卢龙县、青龙县共 8 个区县的 609 家工业企业。调研内容包括企业现场的有组织排放的 VOCs 浓度[采用美国 RAE PGM-7340 高精度 TVOC 检测仪,主要为光离子化(PID)检测器],气体排放流量(采用烟枪进行检测),企业采用的 VOCs 控制技术和工艺、处理效果等。

1.3 数据处理与分析方法

采用分类统计方法分析了不同行业 VOCs 排放源案例数量、产生气体流量、排放浓度和排放速率以及 VOCs 控制技术的市场占有率、适用行业、处理情况等(分析软件采用 Origin 8.5)。

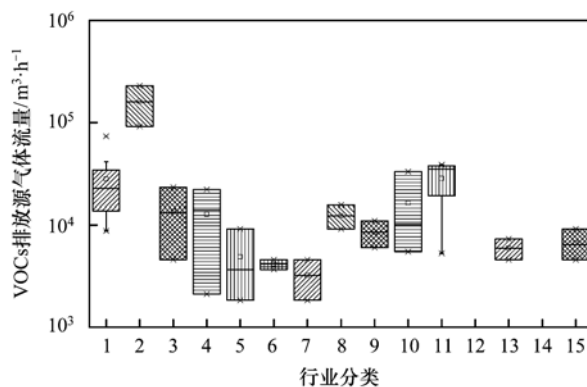
2 结果与讨论

2.1 不同行业 VOCs 排放源气体流量分布

不同行业 VOCs 排放源气体流量分布如图 1 所示。结果表明,秦皇岛市各行业 VOCs(主要为有组织排放源)排放源的气体流量主要集中在 $10^3 \sim 10^5 \text{ m}^3 \cdot \text{h}^{-1}$,只有石油加工、炼焦和核燃料加工业在 $10^5 \text{ m}^3 \cdot \text{h}^{-1}$ 以上。其次为交通运输设备制造业和化学原料和化学制品制造业。与全国的调查研究相比^[21],医药制造、有机化工(塑料及橡胶)以及钢铁冶炼和压延加工行业排放情况相对比较吻合,其他行业都有一定的差异,尤其是石油加工炼焦和核燃料加工业,差异较为明显。这与企业规模有一定的相关性,秦皇岛市是一个旅游城市,因此石油加工类企业相比全国范围内的企业规模要相对较小一些。

2.2 不同行业 VOCs 排放源气体浓度分布

不同行业 VOCs 排放源气体浓度分布如图 2 所示。结果表明,秦皇岛市各个行业的 VOCs 浓度分布主要在 $100 \sim 600 \text{ mg} \cdot \text{m}^{-3}$,其中 VOCs 的浓度较高的行业主要是交通运输设备制造业、石油加工、炼焦和核燃料加工业、机械设备制造业、印刷和记录媒介复制业及化学原料和化学制品制造业,排放浓度均值高于 $400 \text{ mg} \cdot \text{m}^{-3}$ 。但是这几个行业浓度范围



1. 交通运输设备制造业, 2. 石油加工、炼焦和核燃料加工业, 3. 机械设备制造业, 4. 印刷和记录媒介复制业, 5. 其他, 6. 玻璃制造业, 7. 电子及通信设备制造业, 8. 塑料制品业, 9. 金属制品业, 10. 其他制造业, 11. 化学原料和化学制品制造业, 12. 食品制造业及酒类制造业, 13. 皮革、毛皮、羽毛及其制品和制鞋业, 14. 环境治理业, 15. 机械和设备修理业及农副产品加工业, 下同

图 1 秦皇岛市不同行业 VOCs 排放源排放气体流量分布

Fig. 1 Flowrate distribution of VOCs gases from different industries in Qinhuangdao City

也较广,这与检测时段、生产工艺、企业规模以及 VOCs 收集系统有关。而其他行业所排放的 VOCs 排放浓度均较低,均在 $100 \text{ mg} \cdot \text{m}^{-3}$ 以下。这与全国的调查研究具有一定的差异性^[21],全国工业企业 VOCs 排放浓度集中在 $10^2 \sim 10^4 \text{ mg} \cdot \text{m}^{-3}$ 之间,秦皇岛市工业企业排放的 VOCs 浓度较全国而言相对较低。因为秦皇岛市属于新兴的工业城市,工业企业规模和全国范围内调查研究的对象有一定的差距。

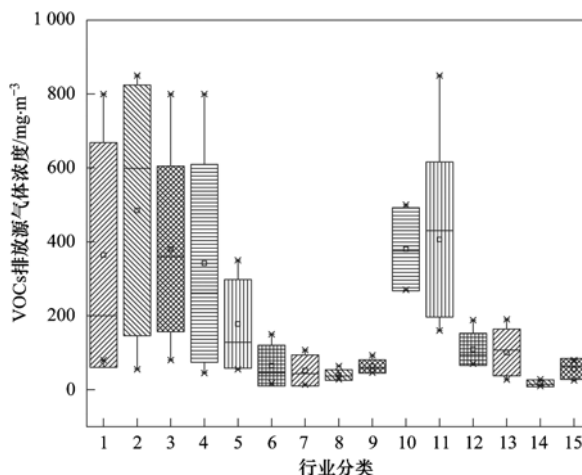


图 2 秦皇岛市不同行业 VOCs 排放源排放浓度分布

Fig. 2 Emission concentration of VOCs gases from different industries in Qinhuangdao City

2.3 不同行业 VOCs 排放源速率分布

不同行业 VOCs 排放源的排放速率分布见图 3。结果表明,秦皇岛市工业行业的 VOCs 排放速率均

在 $50 \sim 10\,000 \text{ g} \cdot \text{h}^{-1}$ 之间,其中交通运输设备制造业、石油加工、炼焦和核燃料加工业、机械设备制造业与印刷和记录媒介的复制业排放速率较高,大多数在 $500 \text{ g} \cdot \text{h}^{-1}$ 以上. 而玻璃制造业、电子及通信设备制造业和塑料制品业排放速率则较低,主要由于玻璃制造业、电子及通信设备制造业的生产过程中溶剂的使用量较小,塑料制品业 VOCs 排放源于挤塑和热熔过程中的挥发泄漏,排放速率均相对较

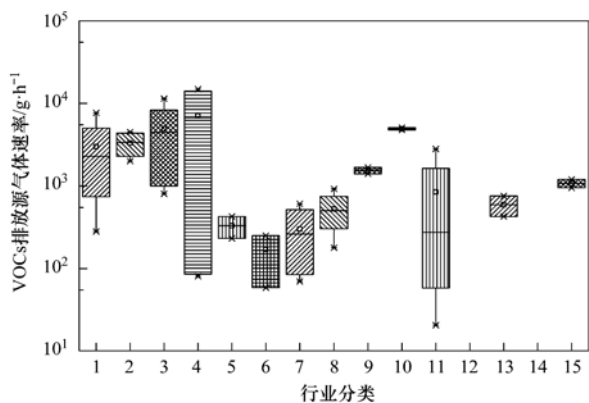
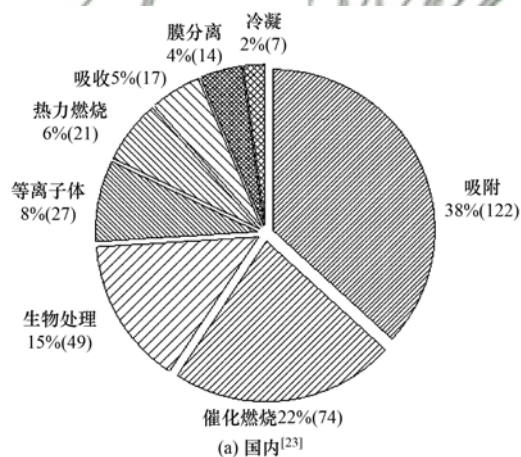


图3 秦皇岛市不同行业 VOCs 排放源排放速率分布

Fig. 3 Emission rate of VOCs gases from different industries in Qinhuangdao City



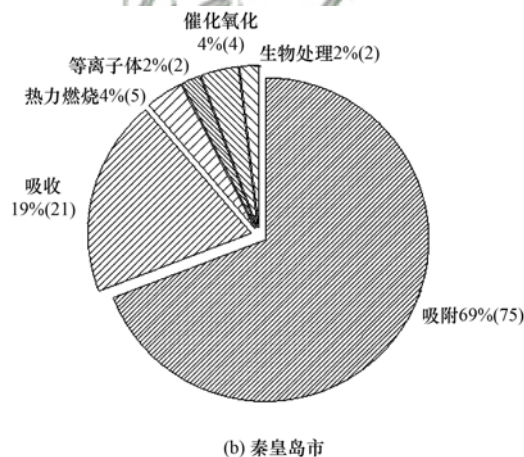
(a) 国内^[23]

小. 这之前王铁宇等^[22]的研究有一定的吻合性,石油加工及炼焦行业、机械设备制造业和印刷行业的排放呈现出风量较大、浓度较高的排放水平,而电子制造业则排放速率较低. 这主要与不同行业的生产工艺有关.

3 秦皇岛市工业 VOCs 处理技术应用现状

3.1 不同 VOCs 处理技术在工程案例中所占比例

统计了不同 VOCs 处理技术在秦皇岛市工程案例中的占比,并与国内研究做对比,结果见图4所示. 秦皇岛市和国内其他地区具有显著差异. 秦皇岛以吸附技术应用占比较高,达到 69%. 其次为吸收技术,为 19%. 其余技术的市场占有率都相对较低. 而从全国范围上来看^[23], VOCs 处理技术在工程案例中的应用主要是吸附法、催化燃烧以及生物法. 主要是因为吸附技术具有能回收 VOCs、操作简便、运行成本较低的特点,因此被广泛应用在工业 VOCs 气体处理当中^[24]. 但是在调查中,企业使用吸附技术过程也存在一些问题,例如吸附剂的更换、设备的维修和吸附剂的处理等,这与高宗江等^[25]的研究结果是一致的.



(b) 秦皇岛市

图4 不同 VOCs 处理技术在国内和秦皇岛市工程案例中所占比例

Fig. 4 Proportion of different VOCs treatment techniques in China and Qinhuangdao City engineering cases

3.2 不同 VOCs 处理技术所处理的气体流量分布

如图5所示,在国内地区 VOCs 处理技术的流量应用范围较广的处理技术有吸附、催化燃烧和生物法^[23],冷凝和膜分离技术受冷凝器和膜分离组件的工作原理限制,只能用于流量小于 $3\,000 \text{ m}^3 \cdot \text{h}^{-1}$ 的 VOCs 气体处理. 调研结果显示,秦皇岛的工业企业多采用活性炭吸附技术,技术应用较为单一. 另外,吸收、吸附、催化燃烧、热力燃烧和等离子体技术处理 VOCs 流量与国内其他地区相同技术案例处

理 VOCs 流量在相同范围内.

3.3 不同技术处理气体的 VOCs 浓度分布

如图6所示,不同 VOCs 处理技术所处理气体的浓度(以 TVOC 计)在国内地区应用差异较大,冷凝法和膜分离法处理的 VOCs 浓度较其他处理技术而言要高一些;等离子体、吸收主要应用于总挥发性有机物(TVOC)浓度小于 $500 \text{ mg} \cdot \text{m}^{-3}$ 的低浓度气体^[23]. 秦皇岛市处理技术应用现状和国内其他地区区别明显,这主要是因为秦皇岛市排放源浓度范

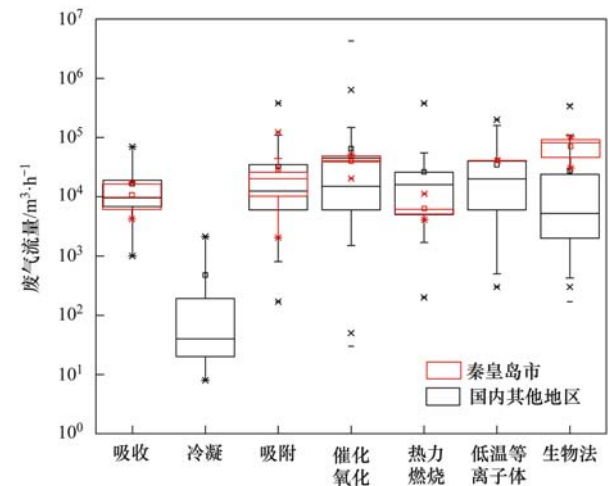


图5 不同处理技术在国内外和秦皇岛市的工程案例所处理 VOCs 气体流量分布

Fig. 5 Flow rate distribution for VOC gases treated by cases based on different techniques in China and in Qinhuangdao City

围相对集中(基本都在 $1\,000\text{ mg}\cdot\text{m}^{-3}$ 以内).

3.4 不同 VOCs 处理技术的行业应用状况

对秦皇岛市 VOCs 处理工程所应用的行业进行归类统计,分析结果如表1所示. 秦皇岛市工业企

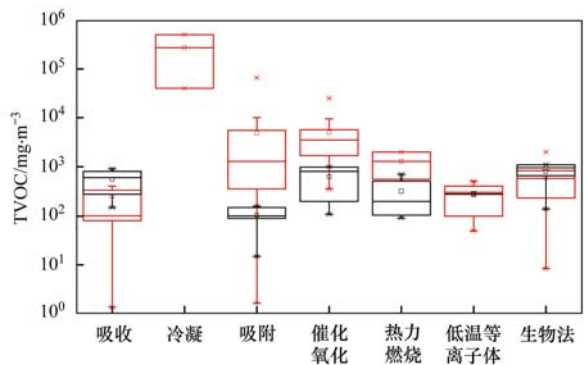


图6 不同处理技术在国内外和秦皇岛市的工程案例所处理的气体 TVOC 浓度分布

Fig. 6 TVOC distribution for VOCs gases treated by cases based on different techniques in China and Qinhuangdao City

业 VOCs 处理的技术,以吸附技术应用的行业最为广泛,其次为吸收技术,其他技术应用案例则较少. 与国内调查研究结果相比差异明显^[23],国内以吸附、催化燃烧、热力燃烧、生物处理在 VOCs 处理方面所应用的行业最广泛. 不同行业的排放特征不同,处理技术的选择也应该有所差异.

表 1 秦皇岛市不同技术工程案例所处理的 VOCs 种类统计¹⁾

Table 1 Number of cases based on different techniques for different target VOCs groups in Qinhuangdao City

行业	不同 VOCs 处理技术应用					
	吸收	吸附	催化燃烧	热力燃烧	等离子体	生物处理
石油加工、炼焦和核燃料加工业	●	●	○	○	○	●
化学原料及化学制品制造业	●	●	○	●	●	○
金属制品业	○	●	○	●	○	○
玻璃制造业	○	●	○	○	●	○
机械设备制造业	●	●	○	○	○	○
交通运输设备制造业	●	●	●	○	○	○
电子及通信设备制造业	○	●	○	○	○	○
塑料制品业	●	●	○	○	○	○
其他制造业	●	●	○	●	○	○
机械和设备修理业及农副食品加工业	●	●	○	○	○	○
食品制造业及酒类制造业	○	●	○	○	○	○
印刷和记录媒介复制业	○	●	○	○	○	○
皮革、毛皮、羽毛及其制品和制鞋业	○	●	○	●	○	○
环境治理业	○	○	○	○	○	●
其他	○	●	○	○	○	○

1) ○表示无案例, ●表示有案例

4 结论

(1)秦皇岛市各行业 VOCs 排放源的气体流量主要集中在 $10^3 \sim 10^5\text{ m}^3\cdot\text{h}^{-1}$,只有石油加工、炼焦和核燃料加工业,在 $10^5\text{ m}^3\cdot\text{h}^{-1}$ 以上. 浓度分布主要在 $100 \sim 600\text{ mg}\cdot\text{m}^{-3}$,排放速率均在 $50 \sim 10\,000\text{ g}\cdot\text{h}^{-1}$ 之间. 交通运输设备制造业、石油加工、炼焦

和核燃料加工业、机械设备制造业、印刷和记录媒介复制业及化学原料和化学制品制造业,这些行业的排放浓度和排放速率均较高.

(2)秦皇岛市工业企业 VOCs 处理技术应用以吸附技术为主,占到 69%. 其次为吸收技术,其他技术应用较少. 吸附技术和吸收技术在秦皇岛市应用流量、浓度范围都较广,行业应用也十分广泛.

(3)与国内地区相比,秦皇岛市工业企业 VOCs 源排放整体水平较低, VOCs 处理技术应用情况较为单一。

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