PAPER • **OPEN ACCESS**

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To cite this article: Guangxun Liu *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **227** 062037

VOCs emission from an important industrial park in Tianjin, China

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Abstract. Volatile organic compounds (VOCs) monitoring methods and monitoring plan is established, and typical large factories in eight industries (petroleum refining and petro chemistry, automobile manufacturing, printing and packaging printing, surface coating, furniture manufacturing, paint and ink manufacture, rubber manufacture and pharmaceutical research lab) in the important industrial zone in Tianjin (China) were surveyed and monitored. The monitoring data indicated that the main VOCs for most industries were BTEX, ester compounds, and methyl isobutyl ketone. VOCs concentrations of petroleum refining and petro chemistry, automobile manufacturing, and surface coating were at a high concentration levels (above 60 mg/m3) and exceed the emission control standard limit. The emission concentration of VOCs was successfully decreased by using the raw material and process that had low release of VOCs and efficient waste gas treatment facilities.

1. Introduction

Volatile organic compounds (VOCs) are one of the main air pollutants, which can be a threat to the environment and human health. Some studies have shown that volatile organic compounds are important precursors of photochemical pollution in the atmosphere, contributing 20% to 50% of $PM_{2.5}$ [1-3]. VOCs pollution control has attracted more and more attention. China has successively issued many policies and regulations to control the pollution emission of VOCs and intensify efforts to control VOCs. It is particularly important to monitor VOCs emissions from industrial facilities in a timely and accurate manner.

The emission control standard for industrial enterprises VOCs of Tianjin was carried out to reinforce the management of VOCs emission in 2014[4]. The emission standard specified the VOCs stationary source emission limits for 10 major industries. As the most important industrial park of Tianjin, Tianjin Economic-Technological Development Area (TEDA) includes many industries that emit large quantities of VOCs, including hydrocarbons (alkanes, olefin and aromatic), ketones, esters, alcohols, phenols, and aldehydes, and many of them are in the *Initial List of Hazardous Air Pollutants with Modifications, EPA*. However, information gaps exist regarding emissions and concentrations of VOCs from the local industrial facilities, which need VOC monitoring programs. The objective of this study is to establish VOCs monitoring procedures get the list of VOCs emissions and magnitude of key industry and key enterprises and prompted them to install waste gas treatment facilities and reduce VOCs emissions.

2. Method and monitoring plan

2.1. Monitoring plan

Monitoring site: Stationary source VOCs monitoring was conducted at typical large factories in eight industries, including petroleum refining and petro chemistry, automobile manufacturing, printing and packaging printing, surface coating, furniture manufacturing, paint and ink manufacture, rubber manufacture and pharmaceutical research lab.

Pre-survey and pre-monitoring: Prior to the formal monitoring, the pre-survey and pre-monitoring of the industries need to be done. In the pre-survey section, the stationary source information was collected, such as the raw materials (MSDS), products, production processes, and waste gas treatment. And in the pre-monitoring section, possible types of substances that may be released were qualitative and concentration levels of VOCs were known. This work had been executed during 2015 and 2016.

Formal monitoring: Flue gas via the waste gas treatment was pumped out by sampling pump from exhaust pipes of those factories and absorbed by the adsorption tube. The frequency of the monitoring was once a season since 2017.

2.2. Monitoring methods

VOCs sampling method includes adsorption tube sampling method, air bag sampling method and absorption tank sampling method, and analysed by gas chromatography (GC) or GC-MS[5-7]. In this programme, the method of VOCs monitoring was sorbent adsorption and the thermal desorption GC-MS, which is a national environmental protection standard of China [8]. The method was referred to TO17 [7], and was determination of volatile organic compounds of stationary source emission sampling by adsorption tube.

Sampling method: The type of the adsorption tube was the mixture of Carbopack C (13mm), Carbopack B (25mm) and Carboxen 1000(13mm) 60-80 mesh, conditioned at 330 ℃ for 2h before use. Sampling flow rate was 50ml/min and last 6min. Replication samples of 10% of sample quantity were taken as the quality control.

Analytical method: (1) Reagent: methanol, VOCs standard substance (Dikma), helium as the carrier gas and dilution gas. (2) Thermal desorption instrument: DANI 1000 STD, desorption temperature 250℃, for 11min, capture trap temperature 0℃ for 2min. valve temperature 220 ℃. (3) Analytical instrument: Agilent GC-MS 6890-5973, HP-VOC column (60m×0.32mm×1.8μm), full scan. (4) Standard curve range's 0.3 mg/m^3-3mg/m^3. VOCs standard solution was injected to Tenax concentrator and analysed by GC-MS.

3. Results and discussion

3.1. The pre-survey and pre-monitoring of the industries

Essential information was got by the pre-survey and pre-monitoring, including raw materials, the main process that produces VOCs, product, emission characteristics, waste gas treatment facilities, and types of VOCs of the different industries (Table 1). VOCs represents substances were usually aromatic hydrocarbons, esters, ketones, and alcohols, Different industries showed different emission characteristics. For example, in the pharmaceutical research lab, there were few kinds of discharges, mainly tetrahydrofuran, and in the automobile manufacturing industry, the process was complex, involving many raw materials and many types of emissions, various types of methyl isobutyl ketone, isobutyl alcohol, xylene and its isomers, trimethylbenzene and its isomers, while the raw materials used in the surface coating industry were mainly esters, xylene, trimethylbenzene and its isomers. The types of VOCs discharged were consistent with the raw materials. The main process that produces VOCs were usually printing, painting, spray, and drying, and the waste gas treatment facilities were regenerative thermal oxidizer (RTO) for high air volume and medium or high concentration, and activated carbon adsorption or low temperature plasma catalysis for low concentration.

Table 1. Information of the pre-survey and the pre-monitoring in the industries (2015~2016)

Industry	Raw materials	The main process that produces VOCs	Product	Emission characteristics	Waste gas treatment facilities	VOCs identified by pre-monitoring
Petroleum refining and petro chemistry	Styrene	Polymerization	Polystyrene	Components of a single	Regenerative thermal oxidizer (RTO)	Styrene
Automobile manufacturing	Epoxy paint Alkyd resin paint Acrylic paint	Automobile painting, drying	Automobile	High air volume, medium or high concentration	Activated carbon adsorption	Methyl isobutyl ketone, isobutyl alcohol, xylene and its isomers, trimethylbenzene and its isomers
Printing and packaging printing	Ink Polyurethane adhesive Water-based adhesive Dilution solvent	Printing	The outer membrane Bowl cover Bag products	High air volume, medium or high concentration	Regenerative thermal oxidizer (RTO)	Ethyl acetate, propyl acetate, butyl acetate, isopropanol
Furniture manufacturing	Solvent based coating Water-based paint	Painting process	Wood furniture	Medium and low air volume, low concentration	Low temperature plasma catalysis	Butyl acetate, ethyl acetate, propylene glycol methyl ether, toluene, xylene, ethylbenzene
Paint and ink manufacture	Butyl acetate Xylene Ethyl acetate Epoxy resin Acrylic resin	Production of coatings (solvent based coatings)	Vanish	Medium high air volume, medium high concentration	Regenerative thermal oxidizer (RTO)	Ethyl acetate, butyl acetate, methyl isobutyl ketone, toluene, xylene
Rubber manufacture	Natural rubber Synthetic rubber	Rubber tightness, vulcanization	Tire	High air volume, low concentration	Spray absorption	2-methylhexane, 3-methylhexane, heptane, n-hexane
Surface coating	Paint Dilution solvent	Spray	Sprayed plastic products	High air volume, medium or high concentration	Activated carbon adsorption	Dimethylbenzene, trimethylbenzene and its isomers, methyl isobutyl ketone, butyl acetate, isopropyl methoxyacetate, ethyl acetate
Pharmaceutical research lab	Dilution solvent	Hydrolysis reaction Addition reaction	Bulk drug	Medium or high air volume, low concentration	Activated carbon adsorption	Tetrahydrofuran, toluene, dichloromethane

3.2. Formal monitoring results

Emission of VOCs represents substances in various industries were shown in Table 2. DB 12/524-2014 is the emission standard of Tianjin, China, and specified the VOCs stationary source emission limits. The limits of different industries are different, and the limits are equivalent to the New Source Performance Standard (NSPS) and 2004/42/EC, looser than the Pollution Prevention and Abatement Handbook 1998.

The VOCs detected obviously were carefully checked and verified with the actual production raw material, types of productive technology and waste gas treatment facilities of the industry, and the result can reflect the emission characteristics under the normal working condition of the industries. The monitoring data of 2017 indicated that the main VOCs for most industries were BTEX, ester compounds, and methyl isobutyl ketone. VOCs concentrations of petroleum refining and petro chemistry, automobile manufacturing, and surface coating were at a high concentration levels (above 60 mg/m^3) and exceed the standard limit. VOCs concentrations of furniture manufacturing, paint and ink manufacture, and pharmaceutical research lab were between 30 mg/m^3 and 50 mg/m^3, while in the factories of printing and packaging printing and rubber manufacture, the VOC emission is of low concentration (below 20mg/m^3).

Table 2 Emission of VOCs represents substances in various industries.

Industry	Substances	Average of VOCs Concentration (mg/m^3)		Sum of VOCs Concentration (mg/m^3)		VOCs emission standard (mg/m^3) (DB 12/524-2014)
		2017	2018	2017	2018	
Petroleum refining and petro chemistry	Benzaldehyde	47.2	0.7	85.6	26.2	80
	Styrene	38.4	25.5			
Automobile manufacturing	m-xylene	14.6	2.8	61.1	13.9	50
	Methyl isobutyl ketone	13.0	2.9			
	Ethyl benzene	11.2	1.5			
	methyl ethyl benzene	10.1	1.3			
	o-xylene	6.1	2.0			
	trimethylbenzene	6.1	3.4			
Printing and packaging printing	Propyl acetate	7.7	4.5	17.2	11.4	50
	Ethyl acetate	6.3	3.9			
	Butyl acetate	3.2	3.0			
Furniture manufacturing	Butyl acetate	12.2	8.2	35.8	31.1	60
	m-xylene	7.1	6.6			
	Sec-butyl acetate	5.7	5.3			
	Propylene glycol monomethyl ether acetate	4.3	4.0			
	toluene	3.9	4.3			
	o-xylene	2.7	2.7			
Paint and ink manufacture	Butyl acetate	26.7	16.4	44.7	24.7	80
	m-xylene	8.7	4.1			
	toluene	3.9	1.6			
	Ethyl benzene	2.8	1.4			
	o-xylene	2.6	1.2			
Rubber manufacture	n-hexane	2.3	1.5	3.6	2.8	10
	3-methylpentane	1.0	1.1			
	methylcyclopentane	0.3	0.2			
Surface coating	Butyl acetate	45.9	11.2	94.2	32.0	60
	Methyl isobutyl ketone	15.6	6.9			
	Isopropyl methoxyacetate	8.5	3.8			
	trimethylbenzene	7.2	2.9			
	Ethyl acetate	6.2	2.8			
	o-xylene	5.5	1.9			
	m-xylene	5.3	2.5			
Pharmaceutical research lab	2-methyl tetrahydrofuran	13.6	8.5	37.0	19.2	40
	Ethyl acetate	9.5	3.1			
	toluene	5.5	2.8			
	Methylene chloride	4.1	2.5			
	2-methyl-2-methoxypropane	2.7	1.3			
	tetrahydrofuran	1.6	1.0			

3.3. Management of VOCs emissions
The aim of supervision is to meet the emissions standards for all the industries and qualitative and quantitative analysis of these representative substances was of great significance. For overqualified enterprises in 2017, the reasons would be analysed to reduce the VOCs emissions. Enterprises that meet the standards should maintain the normal operation of the waste gas treatment facilities and use the raw material and process that had low release of VOCs. For the industry of petroleum refining and petro chemistry, RTO would be well controlled to reduce the benzaldehyde production. Activated carbon adsorption would be replaced by RTO to remove the waste gas of high air volume and high concentration in surface coating and automobile manufacturing industries. The monitoring data of 2018 showed that the measures achieved good results. The emission concentration of VOCs efficiently decreased, and could meet standard requirements.

4. Conclusions
This VOC monitoring campaign depicted the VOC emission characteristics of eight major industries in the most important industrial park in Tianjin, northern China. Practice had proved that the monitoring method of VOCs was effective and the results were credible by comparing with the information of the pre-survey and pre-monitoring. As the emission control standard for VOCs in Tianjin has been carried out for several years, the VOCs emission concentration of enterprises is relatively high. The monitoring data provided evidence for strengthen environmental management, and the emission concentration of VOCs efficiently decreased.

The sorbent adsorption and the thermal desorption GCMS method was suitable for stationary source emission of VOCS. Other methods such as air bag sampling or canister sampling should be studied for monitoring more VOCs. Besides, management of unorganized leaks and monitoring of ambient air shall be carried out in future.

Acknowledgment
This study was funded by: (1) Scientific Research Project of Tianjin Eco-city Investment and Development Co. Ltd. (Grant #: 2017KT08), (2) Tianjin enterprise post-doctoral innovation project preferential funding scheme recommended funding projects (Grant #: TJQYBSH2017025).

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