DEPARTMENT OF ENVIRONMENTAL QUALITY AIR QUALITY DIVISION ACTIVITY REPORT: Scheduled Inspection

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FACILITY: Dow AgroSciences, LLC		SRN / ID: P1028
LOCATION: 701 Washington Street, MIDLAND		DISTRICT: Saginaw Bay
CITY: MIDLAND		COUNTY: MIDLAND
CONTACT: Patty Worden, Senior Environmental Specialist		ACTIVITY DATE: 09/12/2019
STAFF: Kathy Brewer	STAFF: Kathy Brewer COMPLIANCE STATUS: Compliance	
SUBJECT: EU12b and EU03 inspection records review. Facility shut down so will complete site inspection after Sept 24 when control device and associated monitoring can be confirmed. Walkthrough Sept 30. All required monitoring and control devices installed and operating properly.		
RESOLVED COMPLAINTS:		

EU12b and EU03 inspection September 12 and 30, 2019

DAS/Corteva contact: Patty Worden, Senior Environmental Specialist

EU12b is a 2,4-D process unit with manufacturing located in 948 Building. EU03 is a 2,4-D (2,4dichlorophenoxyacetic acid) salt herbicide process with manufacturing equipment located 959 Building. The most recent PTI for EU12b was PTI No. 85-14 and PTI No. 84-14 for EU03. A PTI application No. 108-19 is in house for EU12b.

EU12b and EU03 typically vent to the 963Throx in 963 Building which is currently owned and operated by Dow Dupont (DDP). When the 963THROX is not available process exhaust from EU12b and EU03 can be directed to a carbon adsorber system that is associated with EU12b.

The assets associated with EU12b and EU03 were recently transferred from Dow Chemical SRN A4033 to DAS/Corteva SRN P1028. The emission unit processes remain in the same location and are part of one Stationary Source that is Major for Hazardous Air Pollutants. Both units are subject to the requirements of 40 CFR Part 63, Subparts A, and MMM. In addition, processes subject to MMM are also ubject to the equipment leak provisions of 40 CFR Part 63, Subpart H (National Emission Standards for Organic Hazardous Air Pollutants for Equipment Leaks) as referenced in FGHONFUGITIVES (as specified by 63.1363(b)), as applicable. EU12b is also subject to 40 CFR Part 63, Subpart EEEE

The on site inspection occurred over 2 days. The process was not operating on September 12 but was operating on September 30. The inspection included a review of the process flow diagram, including control devices and vents, on site records, control room process screen, organic wash solvent waste storage, and, ROP required e mission control and metering devices. AQD records were also reviewed.

An April 2018 release of less than 10 pounds of chloroacetic acid from a high line associated with 948 building was reported. No additional direct releases were found post 2016 for EU12b or EU03 in AQD release report database

Based on the site visit and records review the facility appears to be in compliance with the ROP Special conditions for EU12b and EU03.

On Site Records Review

EU12b

July and Feb 2019 963THROX status during unloading for perchloroethylene from tank trucks. April and December 2018, Feb 2019

vent to carbon bed (DO_0002) status 963Throx scrubber (T301) flow 963Throx scrubber (T301) pH 963Throx exhaust temperature T1010 scrubber flow VS-1011 scrubber flow VOC emission calculations Hours carbon adsorber utilized September 2017 calibration of flow meter for scrubber T1010 to VS-1011 January 2018 through August 2019 12 month rolling 963Throx bypass time

∟U03

June and August 2019 vent to 963Throx (DO_0001) status while process operating June 2019 vent to carbon adsorber (DO_0002) status while process operating

AQD File Review

MAERS 2018 emissions

ROP Annual and semi annual Deviation reports September 2017, March 2018, September 2018, March 2019

MACT Reports Subpart MMM and Subpart H, March 2019, September 2019 Permit EVAL forms for 84-14 and 85-14

EU12b

Raw materials are dichlorophenol (DCP) and sodium hydroxide. Raw materials feed a batch reaction followed by continuous flow operation fed by surge tank. The material from the crude storage goes through extraction, followed by purification, steps including acidification and washing. and is then distributed to other site locations.

Filling losses due to material transfer account for much of the process exhaust. A DCP solvent recovery loop handles excess DCP recovered in an extraction step. Process vents are directed to VS-1011/T-1010 caustic scrubber which is exhausted to a knock out pot and condenser whose liquid streams go back into the process and exhaust to the 963Throx or the carbon adsorbers.

Perchloroethylene is used for material recovery from process steps. Perchloroethylene is received by tank truck and stored in a tank. Perchloroethylene storage tank filling losses vent to the 963Throx.

The 963Throx has undergone performance testing which shows it has an organic removal efficiency greater than 99.9%. The carbon adsorber system must meet a PAI MACT removal requirement of 98% for OHAPs. The caustic scrubbers control HCL/CL2 as required under the PAI MACT.

Brine storage tanks contain brine stream residual product recovered from a post 2,4-D extraction wash step and vent directly to atmosphere. Recycle water tanks also vent to 963Throx or carbon adsorbers

The emissions reported to MAERS in 2018 were the following:

Pollutant	Amount
VOC	12 pounds
PM10	0.65 pounds

Supporting documentation for the emission calculations was provided as an attachment in the MAERs submittal.

Emission limits

Review of on site records indicate the facility is in compliance with permitted limits

Pollutant	Limit (12-month rolling time period)	April 2018 (12-month rolling time period)	December 2018 (12-month rolling time period)	February 2019 (12-month rolling time period)
VOC	10 lbs/yr	2.67 lbs/yr	2.66 lbs/yr	2.65 lbs/yr

Material limits

The ROP does not list any specified material limits

ocess and Operational Restrictions

SC III.1 requires the carbon adsorber system meet a PAI MACT removal requirement of 98%. The facility used a design evaluation based on maximum feed rate and available capacity. It was determined that each of the 3 carbon adsorbers can accept vent exhaust for 24 hours. An alarm for change out is set at 23 hours. An "AC" (analog calculation) for carbon bed hours is tracked.

Over the past three years the carbon has been changed between 8 and 11 times in a year. The 3 carbon adsorbers are valved so that one receives vent exhaust and either of the two unused adsorbers are available when needed.

SC III.2 prohibits the facility from starting to unload perchloroethylene from any tank truck unless the 963Throx is operating. Operations data reviewed indicate the site is in compliance with this requirement

Perc offload date	FGTHROX status (temp C)	Valve to throx (DO_0001)
7/17/2019	>750	Open during offload
2/28/2019	>750	Open during offload

Attached are operations data for offloading activity on dates listed above

SC III. 3 limits the hours that process vents from EU12b are exhausted to the carbon adsorber system to 480 per 12 month rolling period. Review of on site records found the hours the process exhausted to the carbon adsorber system to be between 56 and 288 hours (4.7 and 12 days) per 12 month rolling time period. Example operations data are attached.

Jesign and Equipment Parameters

SC IV.1 requires the VS-1011 and T-101 caustic scrubber be equipped with a liquid flow indication device to determine liquid flow to each stage. Annually operators compare total pump outflow from V-1010 caustic scrubber recycle to flow to T-1010 and VS-1011 which both flow into V-1010. The activity is documented in SAP work order. An example work order for 9/6/2017 is attached. During the September 30, 2019 walkthrough the scrubber flow metering devices appeared to be installed and operating properly.

SC IV.2 requires the caustic scrubbers maintain a minimum flow rate that complies with the operating range of 14 gpm for T-101 and 60 gpm for VS-1011 established under the PAI MACT. Monitoring device records and in field observations indicate compliance with the limit

Device	Established operating range flow	Date April 4, 2018	Date December 4, 2018	Date February 4, 2019	Sept. 30, 2019 Instantaneous
VS-1011	60 gpm	100 gpm	100 gpm	100 gpm	99.1
T-1010	14 gpm	18 gpm	18 gpm	18 gpm	17.9

SC IV.3 prohibits the operating of equipment vented to 963Throx or the carbon adsorber unless the control equipment is operating in a satisfactory manner. FG963THROX requires, in part, that the 963THROX operate at a minimum exhaust temperature of 701.4 C and minimum Scrubber 6 liquid flow rate of 79.7 gpm,or, other stack test based limits.

he facility tracks the 963Throx exhaust temp, Scrubber 6 (T301) pH and flow, and valve to carbon adsorber bypass valve (DO_0002) open/closed status. Example 963Throx exhaust temp, Scrubber 6 (T301) pH and flow, and valve to carbon adsorber bypass valve (DO_0002) open/closed status

esting/Sampling

The ROP does not list any specified testing or sampling. In December 2015 a stack test was conducted and established operating ranges for the caustic scrubber system (VS-1011 and T-1010).

Monitoring and Recordkeeping

SC VI.1 requires monitoring and recording of the liquid flow rate for each stage of the caustic scrubber system (VS-1011 and T-101). Records review and on site inspection indicate the facility is in compliance with this requirement.

SC VI.2 requires continuous flow monitoring of the vent to the carbon adsorbers. The valve directing flow to the carbon adsorbers (DI_0002) is monitored and it's status recorded. Attached are operating records showing DI_0002 status for April 4, 2018, December 4, 2018, and February 4, 2019.

SC VI.3 requires the permittee to calculate and record emissions to demonstrate compliance with the VOC limit of 10 lbs/yr. The facility assumes the process operated every day of a month and worst case emissions for 24/7 for any operating time for both periods venting to 963THROX or carbon adsorber system. The established worse case emission rate from air permit application times hours and days in a month is used for emissions estimates. The sum of emissions from carbon adsorber system and emissions from 963TTU for month determined, then the 12 month rolling value is calculated

SC VI.4 requires the permittee to record 12 month rolling hours that process vents from EU12b are exhasuted to the carbon adsorber system. The site combines the periods when EU12b or EU03 are venting to the carbon adsorbers. Review of on site records indicate the facility is in compliance with monitoring requirements

Pollutant	Limit (12-month rolling time period)	April 2018 (12-month rolling time period)	December 2018 (12-month rolling time period)	February 2019 (12-month rolling time period)
Hours vented to carbon adsorber	480 hrs/yr	264 hrs/yr	199 hrs/yr	197 hrs/yr

Reporting

ROP Deviation reports found that in Jan 2016 the T-1010 scrubber flow was between 10 and 12 gpm instead of required 14 gpm on two separate days. The cause is believed due to plugging from buildup of carbonates in scrubbing fluid. Scrubber system began operating in 2015. Actions to prevent the plugging in the future include process control adjustments to reduce carbonate levels and purge quantity adjustments to optimize the carbonate levels in the scrubber fluid.

An ISO container subject to PAI MACT did not receive semiannual inspection required by March 2016.

In May 2017 the 963Throx scrubber had inadequate pH control due to a recirculation pump indicator failure. A VN was written in August 2017 and the issues were resolved by April 2018.

The March and September 2019 Semi Annual PAI MACT reports found no reported instances of excess missions, monitoring downtime, or malfunctions that caused or had the potential to cause an xceedance of any applicable emission standard.

MACES- Activity Report

There was an update to the PAI MACT NOCS to revise the carbon adsorber design evaluation to reflect thehrecent air permit application information. An update was also made to the LDAR equipment counts.

ack/Vent Restrictions

the following vent information was confirmed during the inspection.

Stack & Vent ID	Maximum Exhaust Dimensions (inches)	Minimum Height Above Ground (feet)	Description
1. SV12005 (carbon system atmospheric vent)	4 ²	20 ²	Each of the 3 carbon adsorbers can attach one at time to the vent header

EU03

EU03 is the 2,4-D (2,4-dichlorophenoxyacetic acid) salt herbicide process. Manufacturing equipment is located in the 959 building. The process includes purification of materials followed by reaction vessels. Process condensers and scrubbers are used for material recovery. It is a continuous process. Venting to 963Throx or backup carbon adsorber is mostly from nitrogen purges. Production began in May 2019.

Raw material is offloaded into storage tanks with vapor balance. Purging and filling losses are vented to 963Throx.

Emission limits

ne ROP does not list any specified emission limits. The PTI 84-14 Eval form states that the emissions were far below any relevant thresholds and the nature of the process, raw materials and required emission control equipment adequately limit emissions.

Material limits

The ROP does not list any specified material limits

Process and Operational Restrictions

SC III. 2 limits the hours that process vents from EU03 are exhausted to the carbon adsorber system to 480 per 12 month rolling period. The site combines the periods when EU12b or EU03 are venting to the carbon adsorbers.

Review of on site records found the hours the process exhausted to the carbon adsorber system to be between 56 and 288 hours (4.7 and 12 days) per 12 month rolling time period. Example operations data are attached.

SC III.3 requires that exhaust gases from depressurization of material to the choline hydroxide storage tank be routed to 963Throx or carbon adsorber. The process has not offloaded any railcars yet, only isotainers. The isotainers are gravity feed and the site uses vapor balance when offloading from an isotainer.

Design and Equipment Parameters

SC IV.1 prohibits the operating of equipment vented to 963Throx or the carbon adsorber unless the control equipment is operating in a satisfactory manner. FG963THROX requires, in part, that the 963THROX operate at a minimum exhaust temperature of 701.4 C and minimum Scrubber 6 liquid flow ate of 79.7 gpm, or, other stack test based limits.

MACES- Activity Report

The facility tracks the 963Throx exhaust temp, Scrubber 6 (T301) pH and flow, and valve to carbon adsorber bypass valve (DO_0002) open/closed status. The facility tracks hours of any bypass for -torage vessels exempt to this requirement for up to 240 hours per year under the PAI MACT.

On site review of header vent valve DO_0001 status and choline process operating records indicate the facility is in compliance with this requirement.

Indicator	June 4, 2019 6 - 8 AM	August 4, 2019 4 – 6 PM
Choline process Step 356 status	operating	operating
DO_0001 vent to 963Throx status	open	open

SC IV.2 requires the vapor balance system be operated material is transferred to the choline hydroxide storage tank. The process has not offloaded any railcars yet, only isotainers. The isotainers are gravity feed and the site uses vapor balance when offloading from an isotainer.

Testing/Sampling

The ROP does not list any specified testing or sampling.

Monitoring and Recordkeeping

SC VI.1 requires the permittee to record 12 month rolling hours that process vents from EU03 are exhausted to the carbon adsorber system. The site combines the periods when EU12b or EU03 are venting to the carbon adsorbers. Review of on site records indicate the facility is in compliance with monitoring requirements

Pollutant	Limit (12-month rolling time period)	April 2018 (12-month rolling time period)	December 2018 (12-month rolling time period)	February 2019 (12-month rolling time period)
Hours vented to carbon adsorber	480 hrs/yr	264 hrs/yr	199 hrs/yr	197 hrs/yr

Reporting

The process has only been operating since May 2019. Review of ROP Deviation reports found no EU03 deviations reported. The March and September 2019 Semi Annual PAI MACT reports found no reported instances of excess emissions or monitoring downtime. EU03 was not included and has previously not been included in the Section 11, Table 11 Malfunction Report.

Stack/Vent Restrictions

The following vent information was confirmed during the inspection.

Stack & Vent ID	Maximum Exhaust Diameter/Dimensions (inches)	Minimum Height Above Ground (feet)
1. SV03001 Product storage tank	30 ²	20 ²
2. SV03002 Product storage tank	30 ²	20 ²
	30 ²	15 ²

MACES-	Activity	Report
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3. SV03003 Railcar loading station (from product storage ⁺ank)		
+. SV03004 Railcar loading station (from product storage tank)	30 ²	15 ²
5. SV03005 Railcar loading station (from product storage tank)	30 ²	15 ²
6. SV03006 Railcar loading station (from product storage tank)	30 ²	15 ²

NAME ANT

DATE /10/2009 SUPERVISOR C. Gave