Comments on the proposed standards may be forwarded by email on dinabandhu.cpcb@nic.in and mbalodhi.cpcb@nic.in by February 28, 2018, 05:00 pm.

Executive Summary of Project on "Preparation of COINDS on pharmaceutical industry and Development of Emission standards including VOCs"

1. Introduction

Central Pollution Control Board (CPCB) in consultation with M/s Ramky Enviro Engineers Limited (REEL) initiated a project on "Preparation of COINDS on pharmaceutical industry and Development of Emission standards including VOCs". The Scope of Work is broadly divided into three (3) phases:

Phase – I:	Collection and Collation of Information on Pharma Industry (Dry Study) (*including preliminary field visits to minimum 25 Industries India wide*)
Phase – IIA:	Collection & Collation of Information w.r.t. Pollution Potential Control (*including in-depth field visits to 10 selected industries and sampling/analysis*)
Phase – IIB:	Collection & Collation of Information w.r.t. Pollution Potential & Control (*including in-depth field visits to 5 selected industries and sampling/analysis*)
Phase – III:	Preparation of COINDS and Formulation of Revised Standards

2. Brief Summary of Dry Studies (28 Industries)

For 'Dry Study Report' 28 industries were shortlisted from the four (4) states (Telangana, Tamil Nadu, Gujarat and Maharashtra) for the study. The report presented information including: (a) Overview of pharmaceutical industry in India; (b) Overview of industrial processes in bulk drug manufacturing; (c) Overview of pollution from bulk drug manufacturing industries (d) Inventory of bulk drug manufacturing industries in India and selection of industries for dry studies; (e) Key information from dry studies; (f) Green chemistry; and (g) Findings from 28 industries visited along with CPCB officials as part of 'Dry Study'. The detail study of 28 industries visited during Dry Studies is presented in Dry Study Report.

3. Brief Summary of Wet Study Studies (15 Industries)

For 'Wet Studies' 15 industries were shortlisted from the five (5) states (Telangana, Tamil Nadu, Gujarat, Maharashtra, and Punjab) for in-depth studies. These 15 industries were shortlisted based on (a) production capacity; (b) diversity in the products/therapeutic class (primarily antibiotics, cardiovascular, oncology, analgesics, gastroenterology, and anti-TB drugs etc.); (c) treated effluent discharge method (zero liquid discharge/discharge to CETP etc.); and (d) geographical location etc. Wet Study Report presents the detail study of industries chosen for in-depth/wet studies.

4. Proposed Standards

Table 1: Proposed Standards for Ambient Air

S.No	Solvent Name	Solvent Class[$]	Analysis Results in µg/m³		International Standards					Proposed Standards 24hrs Average in µg/m³
			Min	Max	Canada (Ambient Air) in µg/m³	WHO Guidelines 2000 in µg/m³	EUROPE Ambient air Guideline Value in µg/m³	Thailand Ambient air Guideline Value in µg/m³	New Zealand Ambient air Guideline Value in µg/m³	
1	Benzene	Class 1	0.638	0.638	2.3 (24 hrs) 0.45 (annual)	5 to 20	5 to 20	1.7 (annual)	10 (Annual)	5*
2	Carbon Tetrachloride	Class 1	7.548	8.177	2.4 (24 hrs)	-	-	-	-	7
3	1,2 – Dichloroethane	Class 1	19.85	516.1	105 (24 hrs)	-	-	0.4 (annual)	-	105
4	1,1,1-Trichloroethane	Class 1	43.68	27463.8	115000 (24 hrs)	-	-	-	-	115000[#]
5	Chloroform	Class 2	4.88	341.6	1 (24 hrs) 0.2 (annual)	-	-	0.4 (annual)	-	200
6	Chlorobenzene	Class 2	1.383	46.1	-	-	-	-	-	5
7	Dichloromethane	Class 2	165.6	455.4	220 (24 hrs) 44 (annual)	3000 (24 hrs)	3000 (24 hrs)	22 (Annual)	-	950
8	Trichloroethylene	Class 2	26.85	413.49	12 (24 hrs) 2.3(annual)	-	-	23 (Annual)	-	
9	Methanol	Class 2	524	524	4000 (24 hrs)	-	-	-	-	4,000
10	Cyclohexane	Class 2	67.2	4200	6100 (24 hrs)	-	-	-	-	6,100
11	Xylene	Class 2	0.868	130.2	730 (24 hrs)	4800 (24 hrs), 870 (annual)	4800 (24 hrs), 870 (annual)	-	-	4800

12	Toluene	Class 2	1.508	1.508	2000 (24 hrs)	260 (1 week) 1000 (30min)	260 (1 week) 1000 (30min)	-	-	2,000
13	Ethanol	Class 3	1379.7	15365.7	19000 (1 hr)	-	-	-	-	19,000**
14	Acetone	Class 3	285.6	4688.6	11880 (24 hrs)	0.5 to 125	0.5 to 125	-	-	11,880
15	Isopropyl Alcohol	Class 3	49.2	7724.4	7300 (24 hrs)	-	-	-	-	7,300
16	Ethyl Acetate	Class 3	72	72	19000 (1 hr)	-	-	-	-	19,000**
17	Bromoform	-	51.7	930.6	55 (24 hrs)	-	-	-	-	55
18	Dichlorobenzene	-	6.01	1202	30500 (1 hr)	-	-	-	-	30,500

[$]As per the Residual Solvents USP 46

*Annual Average Value

**1 Hour Average Value

[#] 1,1,1- Trichloroethane is considered as Class A solvent because it is Environmental Hazard as per the Residual Solvents USP 467

Table 2: Proposed Standards for Fugitive Emissions

S.No.	Solvent Name	Solvent Class*	Analysis Results in µg/m³		NIOSH		OSHA		Factories Act, 2015		Proposed Standards
			Min	Max	TWA (ppm)	TWA (µg/m³)	TWA (ppm)	TWA (µg/m³)	TWA (ppm)	TWA (µg/m³)	µg/m³
1	Benzene	Class 1	9.57	31.9	0.1	300	1	3000	10	20,000	20,000
2	Methanol	Class 2	7.86	38173	200	2,60,000	200	2,60,000	200	2,60,000	2,60,000
3	Hexane	Class 2	1235.5	1235.5	50	1,80,000	500	18,00,000	-	-	18,00,000
4	Toluene	Class 2	7.54	6635.2	100	3,75,000	200	7,50,000	100	3,75,000	3,75,000
5	Cyclohexane	Class 2	33.6	2.87	300	10,15,000	300	10,15,000	-	-	10,15,000
6	Dichloromethane	Class 2	20.7	4388.4	25	55,000	25	55,000	-	-	55,000
7	Xylene	Class 2	4.34	34.7	100	4,35,000	100	4,35,000	100	4,35,000	4,35,000
8	Chloroform	Class 2	3416	3416	50	2,40,000	50	2,40,000	10	50,000	50,000
9	Ethanol	Class 3	2457	117066.6	1000	19,00,000	1000	19,00,000	1000	19,00,000	19,00,000
10	Acetone	Class 3	309.4	81991	250	5,90,000	1000	5,90,000	750	17,80,000	17,80,000
11	Ethyl Acetate	Class 3	324	324	400	14,00,000	400	14,00,000	400	14,00,000	14,00,000
12	Isopropyl Alcohol	Class 3	295.2	23443.8	400	9,80,000	400	9,80,000	-		9,80,000

*As per the Residual Solvents USP 46

Table 3: Proposed Standards for Process Vents

S. No.	Solvent Name	Solvent Class*	Analysis Results in µg/m³		Solvent Consumptions for 15 industries		CPCB Standards for Petrochemical Process vents	International Standards for Process Vents			Proposed Standards for Process Vents
			Min	Max	Kg/hr	TPD	mg/Nm³	IFC Guidelines (Pharmaceuticals and Biotechnology Manufactures)	European Countries	California USA	mg/m³
1	Benzene	Class 1	31.9	478.5	1.28	0.33	5	1 mg/Nm³	Total VOC per Vent = 20 mg/Nm³	Total VOC <= 6.8 Kg/day per Industry	5
2	Methanol	Class 2	10467	86460	4357.6	104.6	Nill	Total Class B Solvent - 80 mg/Nm³			50
3	Hexane	Class 2	564.8	99546	1344.5	32.3	Nill				500
4	Toluene	Class 2	11.31	15080000	3110.3	74.65	100				100
5	Cyclohexane	Class 2	100.8	2839200	27.4	0.66	Nill				1000
6	Acetonitrile	Class 2	50.4	1967280	47.5	1.14	Nill				1000
7	Dichloromethane	Class 2	20.7	2825550	1374.5	32.99	Nill				200
8	Xylene	Class 2	4.34	1137080	164.4	3.95	100				100
9	Ethanol	Class 3	1738.8	4541670	471.7	11.32	Nill	Nill			3000
10	Acetone	Class 3	166.6	3929380	1591	38.2	Nill	Nill			2000

11	Ethyl Acetate	Class 3	72	7070400	2126.4	51.03	Nill	Nill			2000
12	Isopropyl Alcohol	Class 3	442.8	5441520	1770.2	42.5	Nill	Nill			2000

***As per the Residual Solvents USP 467**

Table 4: Proposed Standards for Treated Wastewater

S.No.	Parameters	Unit	Proposed Std for final outlet of ETP or ZLD system	Proposed Std for Industries final outlet before discharge to CETP
1.	pH		6.0 -8.5	For each Common Effluent Treatment Plant(CETP), the state Board will prescribe inlet quality Standards for general parameters, Ammonical Nitrogen and Heavy Metals as per the design of the Common Effluent Treatment Plant(CETP) and local needs & conditions.
2.	BOD_3, 27°C	mg/L	30	
3.	COD	mg/L	200	
4.	TOC	mg/L	70	
5.	TSS	mg/L	100	
6.	TDS	mg/L	2100	
7.	Oil & Grease	mg/L	10	
8.	Ammonical Nitrogen	mg/L	50	
9.	Total Kjeldahl Nitrogen	mg/L	50	
10.	Nitrate Nitrogen	mg/L	10	
11.	Phosphates as P	mg/L	5	
12.	Chlorides	mg/L	1000	
13.	Sulphates as SO_4	mg/L	1000	
14.	Fluoride	mg/L	2	
15.	Sulphates as S	mg/L	2	
16.	Phenolic Compounds	mg/L	1	
17.	Total Residual Chlorine	mg/L	1	
18.	Zinc	mg/L	5	
19.	Iron	mg/L	3	
20.	Copper	mg/L	3	
21.	Trivalent Chromium	mg/L	2	
22.	Hexavalent Chromium (Cr^{6+})	mg/L	0.1	
23.	Cyanide	mg/L	0.1	
24.	Arsenic	mg/L	0.2	
25.	Mercury	mg/L	0.01	
26.	Bio - Assay Test	mg/L	90% Suvival of Fish after first 96 hours in 100% effluent	

Table 5: Proposed Standards for VOCs in Treated Wastewater

S.No.	Parameter	USEPA Pharma Standard (Max daily discharge in mg/l)	International Finance Corporation (Effluent Levels for Pharmaceuticals manufacturing in mg/l)	Proposed Standard (mg/l)
1	Benzene	0.05	0.02	0.05
2	Toluene	0.05	0.02	0.05
3	Xylene	0.06	0.01	0.06
4	Methylene Chloride	0.9	0.3	0.9
5	Chlorobenzene	0.15	0.06	0.15
6	Isopropyl Alcohol	3.9	1.6	3.9
7	Methanol	10	4.1	10

5. Summary of Findings

5.1. Ambient Air

Summary of findings (solvent wise) from ambient air including number of readings/samples taken for each individual solvent are presented in **Table 9** below.

Table 6: Summary of Findings – VOCs in Ambient Air

S.No	Solvent Name	Conversion Factor ppm to mg/m^3	Min		Max		Percentile (values in ppm)				Percentile (values in $\mu g/m^3$)			
			ppm	$\mu g/m^3$	ppm	$\mu g/m^3$	75	90	95	98	75	90	95	98
1	Methanol	1.31	0.4	524	0.4	524	0.4	0.4	0.4	0.4	524	524	524	524
2	Ethanol	1.89	0.73	1380	8.13	15366	4.2	7.8	8	8.1	7938	14742	15120	15309
3	Acetone	2.38	0.12	286	1.97	4689	0.7	0.9	1.5	1.8	1666	2142	3570	4284
4	Isopropyl Alcohol	2.46	0.02	49	3.14	7724	1.4	1.9	2.4	2.9	3444	4674	5904	7134
5	Cyclohexane	3.36	0.02	67	1.25	4200	0.2	1.2	1.2	1.2	672	4032	4032	4032
6	Dichloromethane	2.07	0.08	166	0.22	455	0.2	0.2	0.2	0.2	414	414	414	414
7	Carbon Tetrachloride	6.29	0.0012	7.6	0.0013	8.2	0.001	0.001	0.001	0.001	6.29	6.29	6.29	6.29
8	Xylene	4.34	0.0002	0.87	0.03	130	0.03	0.03	0.03	0.03	130.2	130.2	130.2	130.2
9	Chlorobenzene	4.61	0.0003	1.4	0.01	46.1	0.005	0.008	0.01	0.01	23.05	36.88	46.1	46.1
10	1,2 – Dichloroethane	3.97	0.005	20	0.13	516	0.1	0.12	0.12	0.13	397	476.4	476.4	516.1
11	Trichloroethylene	5.37	0.005	27	0.077	414	0.1	0.1	0.1	0.1	537	537	537	537
12	Bromoform	10.34	0.005	52	0.09	931	0.04	0.07	0.08	0.08	413.6	723.8	827.2	827.2
13	Dichlorobenzene	6.01	0.001	6	0.2	1202	0.06	0.1	0.2	0.2	360.6	601	1202	1202
14	1,1,1-Trichloroethane	5.46	0.008	44	5.03	27464	5	5	5	5	27300	27300	27300	27300
15	Chloroform	4.88	0.001	4.9	0.07	342	0.1	0.1	0.1	0.1	488	488	488	488
16	Bromodichloromethane	6.69	0.005	33	0.02	134	0	0	0.1	0.1	0	0	669	669
17	Tertbutylbenzene	5.49	0.01	55	0.09	494	0.1	0.1	0.1	0.2	549	549	549	1098
18	Dibromochloromethane	8.52	0.004	34	0.04	341	0.02	0.03	0.04	0.04	170.4	255.6	340.8	340.8

S.No	Solvent Name	Conversion Factor ppm to mg/m³	Min		Max		Percentile (values in ppm)				Percentile (values in µg/m³)			
			ppm	µg/m³	ppm	µg/m³	75	90	95	98	75	90	95	98
19	Toluene	3.77	0.0004	1.508	0.0004	1.5	0.0004	0.0004	0.0004	0.0004	1.508	1.508	1.508	1.508
20	Ethyl Acetate	3.6	0.02	72	0.02	72	0.02	0.02	0.02	0.02	72	72	72	72
21	Benzene	3.19	0.0002	0.64	0.0002	0.64	0.0002	0.0002	0.0002	0.0002	0.638	0.638	0.638	0.638

5.2. Fugitive Emissions

For the purpose of this study, fugitive emission samples were taken in two methods at each of the 15 industries – (a) Passive Method; and (b) Active Method. For passive sampling method, SKC 575 series passive samplers (with charcoal as sorbent material) were utilized. As per standard guidelines, the passive samplers, after opening the cap, should be clipped to a worker’s collar or shirt pocket as close to the breathing zone as possible (with small holes facing out) and sampling should be carried out for 10 minutes to 8 hours. However, in this case, we slightly modified the guideline and clipped the SKC Passive Sampler to a fixed location within the reactor room close to the breathing zone for 24 hours. We followed the same methodology in all the industries visited for consistency for passive method. For active sampling method, activated charcoal sorbent tubes were utilized along with air sampling pumps. Summary of findings from Fugitive emissions presented in **Table 10** below.

Table 7: Summary of Findings – VOCs in Fugitive Emissions

S.No	Solvent Name	Conversion Factor ppm to mg/m3	Min		Max		Percentile (values in ppm)				Percentile (values in µg/m^3)			
			ppm	µg/m^3	ppm	µg/m^3	75	90	95	98	75	90	95	98
1	Methanol	1.31	0.006	7.9	29.14	38173	15.91	22.87	26.01	26	20842	29960	34073	34060
2	Ethanol	1.89	1.3	2457	61.94	117067	11.65	37.97	49.95	50	22018	71763	94406	94500
3	Hexane	3.53	0.35	1236	0.35	1236	0.35	0.35	0.35	0.35	1235	1235	1236	1236
4	Acetone	2.38	0.13	309	34.45	81991	15.29	26.79	30.62	31	36390	63760	72876	73780
5	Toluene	3.77	0.002	7.5	1.76	6635	0.9	1.42	1.59	1.6	3393	5353	5994	6032
6	Isopropyl Alcohol	2.46	0.12	295	9.53	23444	3.66	7.21	8.37	8.4	9004	17737	20590	20664
7	Cyclohexane	3.36	0.01	34	2.87	9643	0.94	2.1	2.48	2.5	3158	7056	8333	8400
8	Dichloromethane	2.07	0.01	21	2.12	4388	1.2	1.4	1.8	2	2484	2898	3726	4140
9	Chloroform	4.88	0.7	3416	0.7	3416	0.7	0.7	0.7	0.7	3416	3416	3416	3416
10	Xylene	4.34	0.001	4.3	0.008	35	0.01	0.01	0.01	0.01	34.7	34.7	35	355654
11	Ethyl Acetate	3.6	0.09	324	0.09	324	0.09	0.09	0.09	0.09	324	324	324	324
12	Benzene	3.19	0.003	9.6	0.01	32	0.003	0.009	0.01	0.01	9.57	28.7	31.9	32

5.3. Process Vents

Summary of findings (solvent wise) from process vent emissions including number of readings/samples taken for each individual solvent are presented in **Table 8** below.

Table 8: Summary of Findings from Process Vent Emissions (VOCs)

S.No	Solvent Name	Conversion Factor ppm to mg/m3	Process vents				Percentile (values in ppm)				Percentile (values in µg/m³)			
			Min		Max									
			ppm	µg/m³	ppm	µg/m³	75	90	95	98	75	90	95	98
1	Methanol	1.31	7.99	10466.9	66	86460	15	22	36	54	19650	28820	47160	70740
2	Ethanol	1.89	0.92	1738.8	2403	4541670	371	2169	2400	2402	701190	4099410	4536000	4539780
3	Hexane	3.53	0.16	564.8	28.2	99546	3.4	8.1	16.2	23.4	12002	28593	57186	82602
4	Acetone	2.38	0.07	166.6	1651	3929380	464	922	1221	1479	1104320	2194360	2905980	3520020
5	Toluene	3.77	0.003	11.31	4000	15080000	361	2200	3100	3640	1360970	8294000	11687000	13722800
6	Ethyl Acetate	3.6	0.02	72	1964	7070400	1251	1304	1569	1795	4503600	4694400	5648400	6462000
7	Isopropyl Alcohol	2.46	0.18	442.8	2212	5441520	47	642	1120	1740	115620	1579320	2755200	4280400
8	Cyclohexane	3.36	0.03	100.8	845	2839200	59	254	528	723	198240	853440	1774080	2429280
9	Acetonitrile	1.68	0.03	50.4	1171	1967280	176	575	873	1052	295680	966000	1466640	1767360
10	Dichloromethane	2.07	0.01	20.7	1365	2825550	392	1075	1261	1324	811440	2225250	2610270	2740680
11	Xylene	4.34	0.001	4.34	262	1137080	237	252	257	260	1028580	1093680	1115380	1128400
12	NMP	3.48	300	1044000	463	1611240	441	454	458	461	1534680	1579920	1593840	1604280
13	Benzene	3.19	0.01	31.9	0.15	478.5	0.03	0.08	0.1	0.15	95.7	255.2	319	478

In addition to VOCs, other parameters such as PAHs, HBr, HCl, heavy metals were also sampled. Air samples were collected from several process vents from different industries to check for the presence of Heavy Metals (utilizing filter papers). **Table 9** presents the summary of findings related to heavy metal concentration. **Table 10** presents summary of findings related to PAHs, organic particulate matter, HCl and ammonia.

Table 9: Findings from Process Vent Emissions (Heavy Metals)

S.No	Parameters	Units in μg/m^3	
		Min	Max
1	Aluminum as Al	196	2916
2	Antimony as Sb	0.12	3.3
3	Barium as Ba	329.6	1339
4	Cadmium as Cd	0.31	5.2
5	Chromium as Cr	2.5	69
6	Copper as Cu	71	1536
7	Iron as Fe	145	1092
8	Lead as Pb	20	326
9	Manganese as Mn	23	591
10	Nickel as Ni	8.1	318
11	Titanium as Ti	3.7	54
12	Tungsten as W	0.04	0.9
13	Zinc as Zn	134	431

Table 10: Summary of Findings from Process Vent Emissions (PAHs, Organic Particulate Matter, HCl and Ammonia)

Summary of Findings from Process Vents Emissions			
Parameters	Unit	Result	
		Min	Max
Napthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anathracene, Fluoranthene, Pyrene, Benzo (a) anthracene, Chrysene, Benzo (a) fluoranthene, Benzo (a) pyrene, Indeno (1,2,3-cd) pyrene, Dibenz (a,h) anthracene, Benzo (g,h,i) perylene.	μg/m^3	BDL	BDL
Organic Particulate Matter	μg/m^3	70	160
HCl	ppm	2	248.7
Ammonia	μg/m^3	0.1	480

5.1. Wastewater

Most industries visited during dry/wet studies adopted Zero Liquid Discharge (ZLD) systems with different combinations of Stripper/Multiple Effect Evaporator (MEE)/Agitated Thin Film Dryer (ATFD)/Biological Treatment/Reverse Osmosis etc.The main conventional pollutants of concern in wastewater streams from primary manufacturing are biochemical oxygen demand (BOD), chemical oxygen demand (COD), total suspended solids (TSS), ammonia, toxicity, biodegradability, and pH. The chemical compounds that may be present includes solvents such as methanol, ethanol, acetone, isopropanol etc., organic acids such as acetic acid, formic acid, organic halides, ammonia, cyanide, toluene, and Active Pharmaceutical Ingredients (API).

Table 11 below presents wastewater results for conventional parameters discharged to CETP while **Table 12** presents wastewater results for conventional parameters from ZLD. **Table 13** presents wastewater results for presence of active pharmaceutical ingredients and bio-assay test. **Table 14** present wastewater results for solvent in outlet.

Table 11: Summary of Findings – Wastewater discharged to CETP

S.No.	Conventional Parameters	Unit	Inlet Avg	Outlet Avg	Efficiency %
1	pH		8	6.6	
2	Oil & Grease	mg/l	328	21.4	93.5
3	TDS	mg/l	34729	493	98.6
4	Sulphide	mg/l	13	3.7	72.3
5	Bromide as Br^-	mg/l	11	0.7	93.5
6	Residual Chlorine	mg/l	BDL	BDL	0
7	Fluoride as F	mg/l	42	1.4	96.7
8	Carbonate	mg/l	623	10	98.4
9	Phosphates	mg/l	319	1.3	99.6
10	Cyanide as CN	mg/l	BDL	BDL	0
11	Free Ammonia	mg/l	281	12	95.7
12	Ammonical Nitrogen	mg/l	2152	8.7	99.6
13	Total Kjeldhal Nitrogen	mg/l	2312	8.9	99.6
14	Phenols	mg/l	4	1.2	67.3
15	Arsenic as As	mg/l	BDL	BDL	0
16	Chromium as Cr+6	mg/l	BDL	BDL	0
17	Mercury as Hg	mg/l	BDL	BDL	0
18	Lead as Pb	mg/l	0.2	0.1	52.9
19	Cadmium as Cd	mg/l	BDL	BDL	0
20	BOD	mg/l	9865	19.5	99.8
21	COD	mg/l	28706	70.0	99.8
22	TOC	mg/l	16746	11.1	99.9

Table 12: Summary of Findings – Wastewater (Conventional Parameters) from ZLD

S.No.	Parameters	Unit	Inlet Avg	Outlet Avg	Efficiency %
1	pH	-	8	**7**	-
2	Oil & Grease	mg/L	223	7.5	96.6
3	TDS	mg/L	30032	535	98.2
4	Sulphide	mg/L	23	5.7	74.8
5	Bromide as Br -	mg/L	14	0.7	94.8
6	Residual Chlorine	mg/L	BDL	BDL	0
7	Fluoride as F	mg/L	108	4.3	96
8	Carbonate	mg/L	40	22.8	43.4
9	Phosphates	mg/L	464	7.1	98.5
10	Cyanide as CN	mg/L	BDL	BDL	0
11	Free Ammonia	mg/L	342	31.3	90.9
12	Ammonical Nitrogen	mg/L	1565	3.7	99.8
13	Total Kjeldhal Nitrogen	mg/L	205	2	99.1
14	Phenols	mg/L	BDL	BDL	0
15	Arsenic as As	mg/L	BDL	BDL	0
16	Chromium as Cr+6	mg/L	0.3	0.1	78.2
17	Mercury as Hg	mg/L	0.13	0.10	43.6
18	Lead as Pb	mg/L	0.3	0.1	60
19	Cadmium as Cd	mg/L	BDL	BDL	0
20	BOD	mg/L	11167	33	99.7
21	COD	mg/L	36331	147	99.6
22	TOC	mg/L	30547	123	99.6

Table 13: Summary of Findings – Presence of Active Pharmaceutical Ingredients (API) and Bio-assay test

S.No.	Sample Source	Analysis Result	External Laboratories
API Test			
1	Bio-outlet	Absent	Anacon Laboratories, Pro Chem labs
2	RO-I feed	Absent	
3	RO permeate	Absent	
Bio-assay Test			
1	RO outlet	100% survival	Saavanth Envirotech Pvt, ltd.

Table 14: Summary of Findings – Wastewater (Solvents in Outlet)

Parameters	Unit	Results	
		Min	Max
Benzene, Toluene, Xylene, Chlorobenzene, Methyl Chloride, Methanol	ppm	BDL	BDL
Isopropyl Alcoholmn	ppm	0.16	0.35

5.2. Hazardous Waste

About 3 to 4 streams of hazardous waste samples were collected from each industry visited for testing of regular parameters such as flash point, reactivity, toxicity, calorific value etc. and also for testing of absorbable organic halogens (solvents/VOCs) such as chloroform, carbon tetrachloride etc.It is identified from dry studies at 28 industries and wet studies at 15 industries that there is no single stream of hazardous waste which does not fall under Schedule – I of Hazardous Waste (Management, Handling, and Transboundary Movement) Rules – 2008. It is also identified that all industries visited comply with the requirements specified in Consent for Operation (CFO) for management of various streams of hazardous waste.

It is important to quantify organic halogens in hazardous waste, as they may lead to formation of dioxins and furans. Halogenated organics should not be normally incinerated. Where incineration of such organics is required, the **release of dioxins and furans** is restricted to below 1 nanogram per cubic meter, as measured using a toxicity equivalent factor for 2, 3, 7, 8 – TCDD. The results indicated that organic halogen content in hazardous waste from bulk drug manufacturing industry is insignificant.

Summary of findings of absorbable organic halogens in hazardous waste is given in **Table 15**.

Table 15: Summary of Findings - Absorbable Organic Halogens in Hazardous Waste

S.No	Solvent	Min. (in ppm)	Max. (in ppm)
1	1,1,1-Trichloroethane	0.001	3.1
2	1,1,-Dichloroethane	0.0004	0.72
3	1,2,3-Trichloropropane	0.0002	0.002
4	Tetrachloroethane	0.0006	0.08
5	Trichloroethylene	0.0002	0.7
6	Bromoform	0.002	0.14
7	1,1,1,2-Tetrachloroethane	0.0002	0.63
8	Dibromomethane	0.002	0.07
9	1,1,2,2-Tetrachloroethane	0.03	0.11
10	Chloroform	0.0006	26
11	1,1,2-Trichloroethane	0.001	0.18
12	1,2-Dichloropropane	0.0005	0.4
13	1,2-Dichloroethane	0.0007	3332
14	Carbon tetrachloride	0.002	294

6. Control Measures and Methods for Process Vent Emissions

Table 16: List of Control methods for VOCs

S.No	Control Technology	Advantages	Limitations and Contradictions	Working principle	Typical Pre-treatment Consideration
1	**Carbon Adsorption** • Applicable concentration range ppm: 100-2000 • Capacity Range, cfm: 1000-500000 • Removal Efficiency: 96-99% • Secondary waste: Combustion products	Product recovery can offset annual operating costs. Can be used as a concentrator in conjuction with another type of control device. Works well with cyclic process.	Not recommended for streams with relative humidity <50 %. Ketones, aldehydes and esters clog the pores of the carbon, decreasing system efficiency.	In the adsorption process, molecules of a contaminated gas are attracted to and accumulate on the surface of the activated carbon. Carbon is a commonly used adsorbent due to its very large surface area.	Cooling, Dehumidification, dilution, Particulate removal
2	**Absorption** • Applicable concentration range ppm: 100-2000 • Capacity Range, cfm: 2000-100000 • Removal Efficiency: 96-99% • Secondary waste: Combustion product	Product recovery can offset annual operating costs.	Might require exotic scrubbing media. Design could be difficult in the event of lack of equilibrium data. Packing is subject to plugging and fouling if particulates are in the gas stream. Scale formation from adsorbent/adsorber interaction can occur.	Removal of air pollutants by inertial ordiffusional impaction, reaction with a sorbent or reagent slurry, or absorption into liquid solvent.	Cooling, Particulate removal
3	**Biofiltration** • Applicable concentration	Efficient for low	Large amount of space may be required. Microorganisms are	Microorganisms reside on the surface of the biofilter media and	Humidification, Cooling, Particulate

S.No	Control Technology	Advantages	Limitations and Contradictions	Working principle	Typical Pre-treatment Consideration
	range ppm: 100-2000 • Capacity Range, cfm: 1000-50000 • Removal Efficiency: 96-99% • Secondary waste: Combustion products	concentration streams. Low operating costs.	effective only in the 50 to 100°F temperature range and may be killed if proper bed moisture content and pH is not maintained.	only require irrigation water and small quantities of nutrient (for some applications). Microorganisms consume these odorous contaminants for energy and, in the process, cleanse the air.	removal
4	**VOC Concentrators (Rotatory carousel system)** Applicable concentration range ppm: >1000 Waste Gas Flow rate: >283.17 m3/min Removal Efficiency: 90-98%	Efficient for high concentration and low flow rate streams. Low operating costs.	Concentrators produce savings in the size and cost of downstream control equipment. However, a volume concentrator coupled with another control device results in a more complex system, which may affect utility and maintenance requirements.	Volume concentrators are designed specifically for the control of low concentration VOC gas streams. These devices raise the concentration of VOC vapor to allow more economical treatment of concentrated compounds in the exhaust gas.	Cooling, Dehumidification, dilution, Particulate removal
5	**Thermal Oxidation** • Applicable concentration range ppm: 100-2000 • Capacity Range, cfm: 1000-500000 • Removal Efficiency: 96-99% • Secondary wastes: Combustion products	Up to 94% energy recovery is possible	Halogenated compounds may require additional control equipment downstream. Not recommended for batch operations.	The pollutants are destroyed via thermal combustion; they are chemically oxidized to form CO_2 and H_2O. The temperature needs to be high enough to ignite the waste gas. Most organic compounds ignite at the temperature between 590 °C (1,094 °F) and 650 °C (1,202 °F).	Dilution, Preheating
6	**Catalytic Oxidation**	Up to 70%	Thermal efficiency suffers with	Catalytic oxidizers use a catalyst to	Dilution,

S.No	Control Technology	Advantages	Limitations and Contradictions	Working principle	Typical Pre-treatment Consideration
	• Applicable concentration range ppm: 100-2000 • Capacity Range, cfm: 1000-500000 • Removal Efficiency: 96-99% • Secondary waste: Combustion products	energy recovery is possible	swings in operating conditions. Halogenated compounds may require additional control equipment downstream. Certain compounds can poison the catalyst (lead, arsenic, phosphorous, chlorine, sulphur, particulate matter).	promote the oxidation of VOCs to CO_2 and water (i.e., increase the kinetic rate). The catalyst therefore allows oxidation to occur at lower temperatures than for thermal oxidation; catalytic oxidizers generally operate between 650°F and 1000°F.	Particulate removal, Pre-heating
7	**Cryogenic Condensation** • Applicable concentration range ppm: 100-2000 • Capacity Range, cfm: 1000-500000 • Removal Efficiency: 96-99% • Secondary waste: Combustion products	Product recovery can offset annual operating costs	Not recommended for materials with boiling point <100°F. Condensers are subject to scale build up which can cause fouling.	Cryogenic condensation uses liquid nitrogen to control the emission of solvent vapours by taking advantage of the vapour-liquid equilibrium principle of multi-componentmixtures. That is, as the temperature lowered, thesaturation capacity of the carrier gas decreases, causing the concentration of components in the carrier gas to decrease as they condense into liquid droplet.	Dehumidification

7. Solvent Replacement

Special attention has to be paid towards Class 1 solvents as they are known human carcinogens/strongly suspected human carcinogens. Similarly, exposure to Class 2 solvents should be limited. Industries should be encouraged to switch to green chemistry alternatives, especially in case of usage of Class 1 solvents. **Table 17** below presents replacement options for some of the toxic solvents.

Table 17: Replacement Options for some of the Toxic Solvents

S. No.	Red Solvents	Alternative Solvent
1	Pentane	Heptane
2	Hexane (s)	Heptane
3	Di-isopropyl ether or ether	2-MeTHF or t-Butyl methyl ether
4	Dioxane or dimethoxyethane	2- MeTHF or t-Butyl methyl ether
5	Chloroform, dichloroethane or carbon tetrachloride	DCM
6	DMF, NMP or DMAc	Acetonitrile
7	Pyridine	Et_3N (if pyridine used as base)
8	DCM (extractions)/Tetrahydrofuran	EtOAc, MTBE, toluene, 2-MeTHF
9	DCM (chromatography)	EtoOAc/Heptanes
10	Benzene	Toluene

8. LDAR Program

Leaking equipment, such as valves, pumps, connectors, sampling connection, compressors, pressure- relief devices and open end lines are the largest source of emissions of volatile organic compounds (VOCs) and volatile hazardous air pollutants (VHAPs) from chemical manufacturing facilities. Emissions from equipment leaks exceed emissions from storage vessels, wastewater, transfer operations, or process vents.

As per (USEPA LDAR Report), a typical Chemical plant can emit 600-700 tons per year of VOCs from leaking equipment. In a typical facility, most of the emissions are from valves and connectors because these are the most prevalent components and can number in the thousands. The major cause of emissions from valves and connectors is seal or gasket failure due to normal wear or improper maintenance. The program elements were developed from:

- Evaluation of best practices identified at facilities with successful LDAR programs,
- Analysis of the root cause of noncompliance at facility that were found to have recurring violation of LDAR regulatory requirements.

The outlines of some of the major elements of successful LDAR program are mentioned in the below flowchart **Figure 1**. List of components, types of leaks and frequency of monitoring is given below in **Table 18.**

Figure 1: Flowchart of Major Elements of LDAR Program

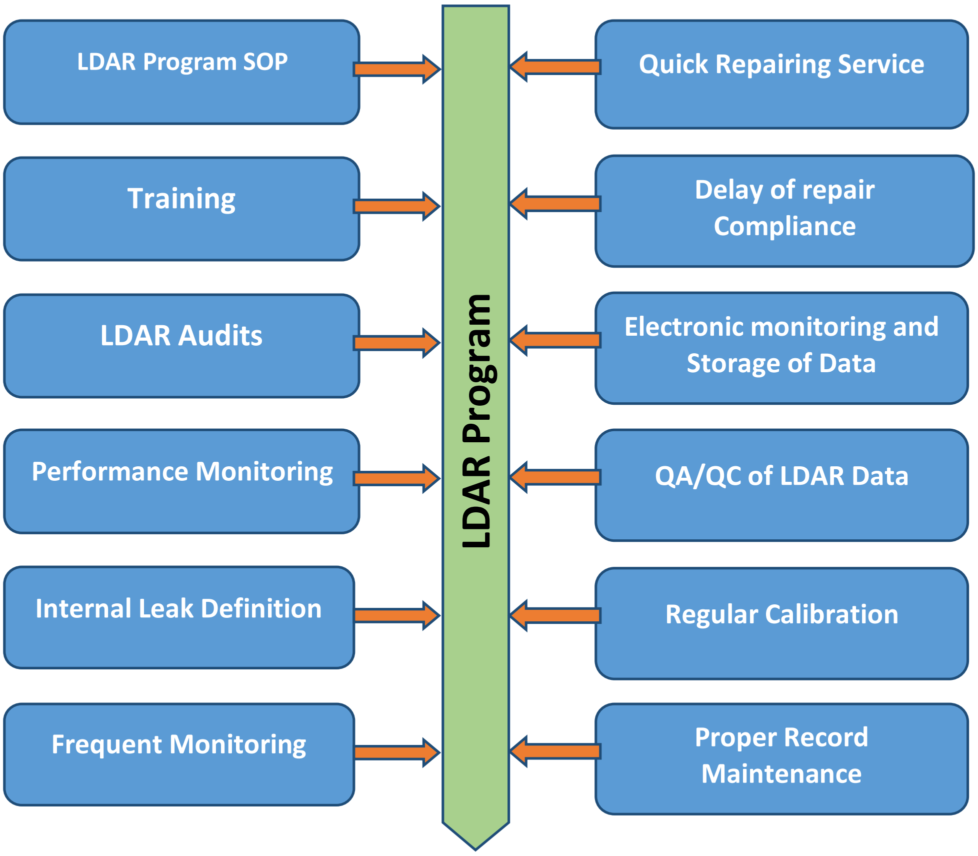

Table 18: List of Components, Types of Leaks and Frequency of Monitoring

S. No	Item of Comparison	Monthly Frequency Monitoring	Types of Leaks
1	Light Liquid valves	• Monthly if >2% leaking • Quarterly if <2% leaking • Every 2 qtrs if < 1% leaking • Every 4 qtrs if <0.5% leaking • Every 2 years if <0.25%	Leaks from valves usually occur at the stem or gland area of the valve body and commonly caused by failure of the valve packing or o- ring
2	Gas Valves	• Monthly if >2% leaking • Quarterly if <2% leaking • Every 2 qtrs if < 1% leaking • Every 4 qtrs if <0.5% leaking • Every 2 years if <0.25%	
3	Gas Pressure Relief Valves	Monitor within 5 days of a release	Leaks from pressure relief valves can occur if the valve is not seated properly, operating too close to the set point, or if the seal is worn or damaged. Leaks from rupture disks can occur around the disk gasket if not properly installed.
4	Liquid Pressure Relief Valves	Monitor within 5 days of detection by sight, smell, or sound	
5	Light Liquid Pumps	Monthly monitor & weekly visual	Occur at the seal.
6	Compressors	Requires a seal system including barrier fluid, sensor, & alarm with zero emissions to atmosphere. Check sensor daily.	Occur at the seal.
7	Flanges/ Connectors	Initial monitorMonitor annually if >0.5% leaking Monitor biennially if <0.5% leaking Monitor every 4 years if <0.5% leaking for 2 years HL connectors: Monitor within 5 days of detection by sight, smell, or sound	Leaks from connectors are commonly caused from gasket failure and improperly bolts on flanges.
8	Heavy Liquid Equipment	Monitor within 5 days of detection by sight, smell, or sound. Repaired systems do not require monitoring	
9	Closed Vent Systems	Hard piping: Initial monitoring annual visual Duct Work:Annual monitor	
10	Open-ended valves/lines	Requires cap, plug, blind flange, or 2nd valve	Leaks from open-ended lines occur at the point of the line open to the atmosphere and are

S. No	Item of Comparison	Monthly Frequency Monitoring	Types of Leaks
			usually controlled by using caps, plugs, and flanges. Leaks can also be caused by the incorrect implementation of the block and bleed procedure.
11	Sampling Points/ Connections	Requires closed purge, closed loop, or closed vent system, Return or recycle purge	Leaks from sampling connections usually occur at the outlet of the sampling valve when the sampling line is purged to obtain the sample.
12	Agitators	Monthly monitor & weekly visual	
13	Surge Control Vessels and Bottoms Receivers	Requires closed vent system	
14	Visual Leaks	Monitor within 5 days of detection by sight, smell, or sound	
15	Instrument-ation Systems	Monitor within 5 days of detection by sight, smell, or sound	