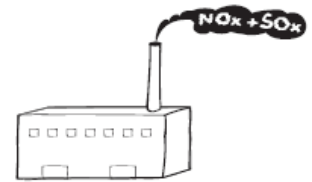


ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

A tool for understanding environmental decisions related to the pulp and paper industry



EMISSIONS TO AIR

EFFECTS OF DECREASED RELEASE OF CHLORINATED COMPOUNDS ON EMISSIONS TO AIR

Emission Levels and Controls Regulatory Backdrop

Bleach Plant: Bleaching system standards for the U.S. are illustrated in Figure C14.

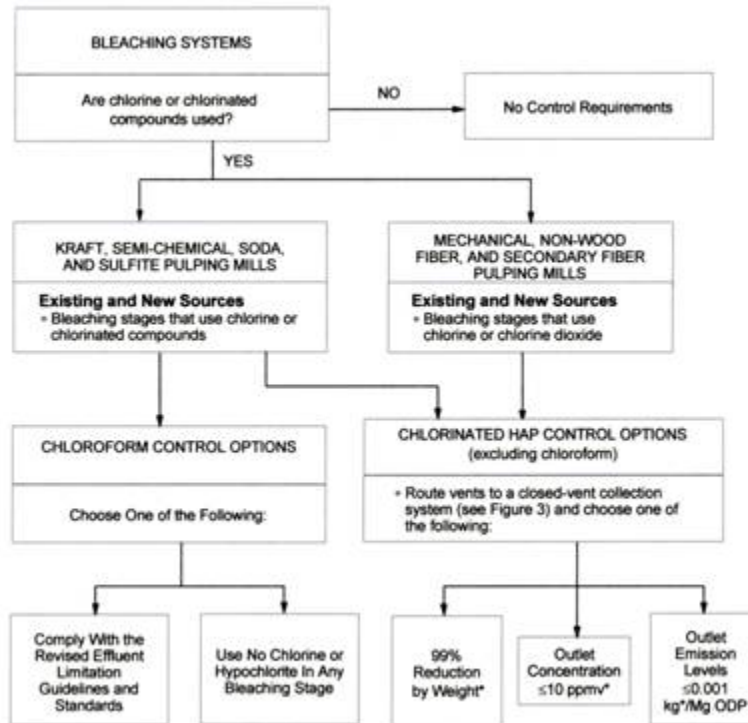


Figure C14. U.S. Environmental Regulatory Standards for Bleach Plants
(Source: USEPA 1997)

U.S. emission standards promulgated in 1998 for chemical pulping require the collection and treatment of all vent gases from the bleaching stages where chlorinated compounds are applied. Treatment to remove chlorine and other gaseous hazardous air pollutants (HAPs) containing chlorine (other than chloroform) is necessary. A mill can demonstrate compliance with the treatment portion of regulation using any one of three alternatives:

- reducing the total chlorinated HAP mass in vent streams by 99% or more, measured as chlorine, using a control device (e.g., a scrubber), or
- reducing the total chlorinated HAP emission concentration (excluding chloroform) to 10 ppmv or less exiting a treatment/control device, or
- reducing the total chlorinated HAP mass emission rate to 0.001 kg total HAP (excluding chloroform) per tonne ODP.

Effects of Decreased Release of Chlorinated Compounds on Emissions to Air *Emission Levels and Controls*

Similar requirements exist for mechanical pulping and secondary fiber mills where chlorine or chlorine dioxide is used.

Chloroform emissions from chemical pulp bleaching are addressed by eliminating use of chlorine and sodium hypochlorite in bleaching sequences.

Emissions from bleach plant sources are commonly treated using scrubbers, typically packed towers. Scrubbing mediums include chilled water, caustic, extraction stage filtrate, sodium bisulfite, weak wash from the kraft recovery causticizing system, hydrosulfite, and white liquor. The effectiveness of these scrubbers is dependent on their design and choice of scrubbing medium. The control efficiency for both chlorine and chlorine dioxide is typically 95% or greater, and achieving greater than 99% efficiency is not uncommon. Thus, while it is likely that in replacing chlorine with chlorine dioxide overall industry emissions of chlorine have decreased and chlorine dioxide emissions have increased, the change in the mass of emissions is small because source controls are very effective.

Oxygen Delignification Sources: Regulations in the U.S. require the collection and treatment of the vent gases from blow tanks, washers, filtrate tanks, and intermediate stock chests that are part of an oxygen delignification system. The specified level of treatment is at least 98% for all gaseous organic "hazardous air pollutants," although demonstrating 98% efficiency for methanol alone is sufficient. Most mills with oxygen delignification systems meet this requirement by ducting the vent gases into a high volume low concentration (HVLC) gas system and introducing the collected gases to a boiler or recovery furnace as combustion air (NCASI 2004).

Bleaching of (Virgin) Chemical Pulps

Until the 1990s, most chemical pulp mills used chlorine and chlorine dioxide to bleach pulp, and some mills also used hypochlorite. The discovery that dioxin can be formed when chlorine is used to bleach chemical pulps led to changes in the chemicals used for pulp bleaching. The most notable change was the elimination of chlorine and hypochlorite in favor of chlorine dioxide in the sequence, known as elemental chlorine free (ECF) bleaching. This conversion also led to the increased use of oxygen and hydrogen peroxide in the bleaching sequence. Complete elimination of all chlorine compounds in pulp bleaching in favor of oxygen and peroxide is termed totally chlorine free (TCF) bleaching.

Air emissions from bleaching that are known to be affected by use of the various bleaching chemicals include chlorine, chlorine dioxide, chloroform, carbon monoxide, and methanol.

Chlorine and chlorine dioxide emission points include bleaching tower vents, bleach plant washer and filtrate tank vents, and the chlorine dioxide generator. Uncontrolled bleach plant emissions of chlorine and chlorine dioxide range from 0 to 10.42 lb/ADTP and from 0.03 to 25.5 lb/ADTP, respectively (NCASI 1991). Uncontrolled emissions from chlorine dioxide generators range from 0.04 to 24 lb Cl₂/ton ClO₂ generated and from 0.2 to 6.12 lb ClO₂/ton ClO₂ generated (NCASI 1991).

Chloroform is a by-product of bleaching with hypochlorite, chlorine and, to a much lesser extent, chlorine dioxide. Oxygen, peroxide, or other non-chlorinated bleaching chemicals do not produce chloroform. Figure C15 has been derived from various NCASI studies. It shows the magnitude of chloroform generation from a typical bleach line using chlorine and hypochlorite relative to a typical line using only chlorine dioxide (ECF). Liquid effluents are included because chloroform in effluent would likely be released to air during wastewater treatment. Chloroform releases from the bleach plant directly to air are of a similar magnitude to effluent loads for these bleaching methods. As is apparent in the figure, 99.5% of the reduction in chloroform emissions has been achieved through implementation of ECF bleaching. The remaining 0.05% reduction could be achieved through TCF bleaching. TCF bleaching is not known to generate chloroform.

Effects of Decreased Release of Chlorinated Compounds on Emissions to Air
Emission Levels and Controls

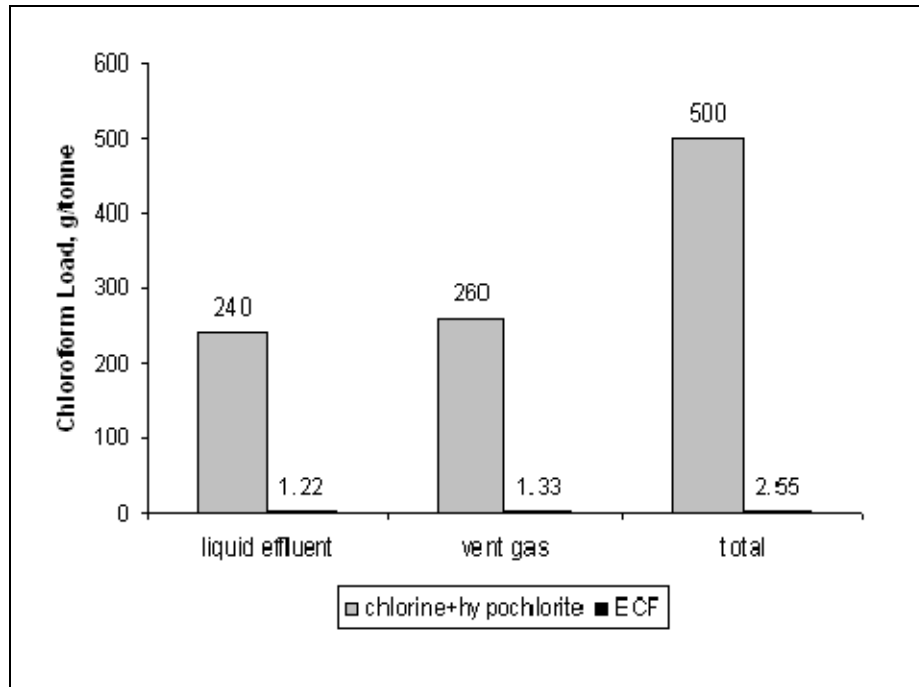


Figure C15. Chloroform Load from Chlorine + Hypochlorite and Chlorine Dioxide (ECF) Bleaching of Kraft Pulp

Carbon monoxide is formed by the use of oxygen in pulping and bleaching, as well as by chlorine dioxide use in bleaching (Dence and Reeve 1996). Increases in the use of both process chemicals as replacements for chlorine have resulted in increased emissions of carbon monoxide, though at some U.S. mills increases due to the use of oxygen delignification may be offset by the use of vent gas control devices.

The mechanisms by which carbon monoxide is formed are not well understood and thus, it is not known whether elimination of chlorine dioxide (for TCF sequences) and expanded use of oxygen and peroxide in the bleaching sequence would result in an increase in carbon monoxide emissions from bleaching.

Methanol is formed in pulping and bleaching (Dence and Reeve 1996). Liquid methanol is also used as a raw material by some mills in the process of generating chlorine dioxide. Emissions of methanol associated with the manufacture and use of chlorine dioxide would be expected to increase as more chlorine dioxide is used to replace chlorine in the bleaching sequence. The relationship between methanol emissions and the increased use of chlorine dioxide and oxygen for bleaching is not straightforward. Data suggest that emissions will be similar for chlorine-based and ECF bleaching (Dence and Reeve 1996). Methanol emission data from TCF sequences are not available but would likely be equal to, or greater than ECF emissions.

Methanol is also prominent among the hazardous air pollutants (HAPs) and volatile organic compounds (VOCs) emitted from oxygen delignification systems common in enhanced ECF and TCF systems, with the release points shown in Figure C16.

Effects of Decreased Release of Chlorinated Compounds on Emissions to Air
Emission Levels and Controls

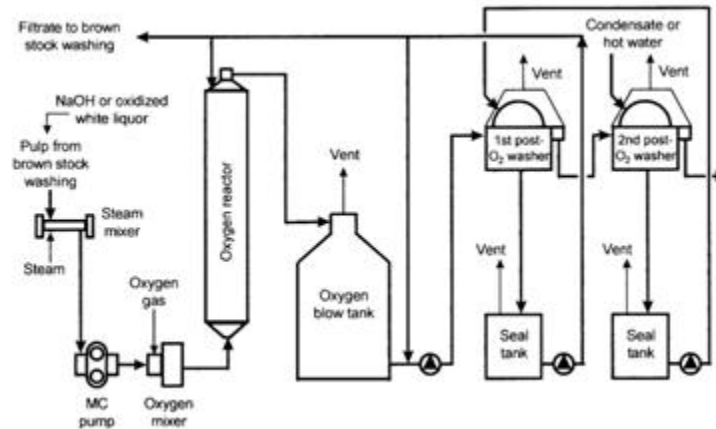


Figure C16. Oxygen Delignification-Related VOC Release Points

Volatile Organic Compounds (VOCs): In mills that practice oxygen delignification, volatile organic compounds present in the incoming pulp slurry, oxidized white liquor, and washer shower water can be released in vent gases from the blow tank, washer hood, washer filtrate tank, and pulp storage tank. The amounts of these compounds present in the various process liquids will depend upon the water reuse practices of the mill, particularly if condensates are used on the post-oxygen washers (NCASI 2008). Data assembled by the Paper Task Force (Table C8) are illustrative.

**Table C8. VOC Emissions from Bleached Kraft Mill Sources
 (Source: Paper Task Force 1995)**

	VOC Emissions	Pulp Mill Sources, (lb C/ODTP)
Conventional Case^a	Pulping	1.11
	Bleaching	0.31
	Chemical Recovery	0.97
	Total	2.39
Traditional ECF	Pulping	1.11
	Bleaching	0.03
	Chemical Recovery	0.97
	Total	2.11
Enhanced ECF^{b,c}	Pulping	1.11
	Bleaching	0.68 (0.15)
	Chemical Recovery	0.96
	Total	2.92 (2.24)

^a Conventional case employs 50% chlorine dioxide substitution.

^b Bleaching sources include the oxygen delignification system and the bleach plant.

^c Values in parentheses include emissions from an oxygen delignification system that used fresh shower water.

Effects of Decreased Release of Chlorinated Compounds on Emissions to Air
Emission Levels and Controls

Though enhanced ECF may be beneficial from the standpoint of organochlorine generation, these data indicate that uncontrolled VOC emissions will be greater than those for traditional ECF. Moreover, VOC emissions from the oxygen delignification system and bleaching sources in enhanced ECF bleaching are more than four times greater when condensates are used in lieu of fresh water.

Other Hazardous Air Pollutants: In 1995, the Paper Task Force assembled data collected by NCASI that quantified uncontrolled emissions of hazardous air pollutants (HAPs) from major bleached kraft mill non-combustion sources. The data are summarized in Table C9.

Table C9. HAP Emissions from Bleached Kraft Mill Sources
(Source: Paper Task Force 1995)

	HAP	Pulp Mill Sources, (lb/ODTP)	Bleach Plant Sources, (lb/ODTP) ^{a,b}	Ratio of Bleach Plant to Pulp Mill Sources
Conventional Case^c	Methanol	2.18	0.52	23.8%
	Acetaldehyde	0.08	0	0.0%
	Formaldehyde	0.02	0	0.0%
	Chloroform	0.13	0.12	92.3%
	Total	2.54	0.68	26.7%
Traditional ECF	Methanol	1.912	0.25	13.1%
	Acetaldehyde	0.085	0.003	3.5%
	Formaldehyde	0.019	0	0.0%
	Chloroform	0.021	0.011	52.4%
	Total	2.132	0.27	12.7%
Enhanced ECF	Methanol	2.932 (2.182)	1.27 (0.52)	43.3% (23.8%)
	Acetaldehyde	0.128 (0.094)	0.047 (0.012)	36.7% (12.7%)
	Formaldehyde	0.021 (0.020)	0.002 (0.00)	9.5% (0.0%)
	Chloroform	0.013 (0.014)	0.002 (0.002)	15.4% (14.3%)
	Total	3.193 (2.402)	1.329 (0.54)	41.6% (22.5%)
Low Effluent TCF	Methanol	2.338	0.135	5.8%
	Acetaldehyde	0.111	0.029	26.1%
	Formaldehyde	0.041	0.021	52.2%
	Chloroform	0	0	0.0%
	Total	2.596	0.158	6.1%

^a Bleach plant sources include the oxygen delignification system and the bleach plant.

^b Values in parentheses include emissions from an oxygen delignification system that used fresh shower water.

^c Conventional case employs 50% chlorine dioxide substitution.

Chloroform and methanol have both been previously discussed. Reduced reliance on chlorine and chlorine dioxide results in less chloroform generation. However, reductions are small in going beyond 100% chlorine dioxide substitution.

For traditional and enhanced ECF sequences, methanol represents greater than 92% of HAP emissions. Methanol content of the evaporator condensates used as wash water on the final stage of post-oxygen washing is the most important factor affecting oxygen delignification system HAP emissions (NCASI 2008). The second most prevalent HAP is acetaldehyde, which contributes about 3% of the total HAPs, on average.

Effects of Decreased Release of Chlorinated Compounds on Emissions to Air *Emission Levels and Controls*

What most distinguishes the low effluent TCF sequence in the assembled data is the mill use of bleach plant filtrate in the first oxygen washer. It suggests that use of TCF sequence filtrates can result in lower HAP emissions than use of condensates.

Brightening of Mechanical and Chemi-Mechanical Pulps

Mechanical and chemi-mechanical pulps are typically bleached (brightened) using peroxide and/or sodium hydrosulfite or other non-chlorine containing chemicals (Dence and Reeve 1996). Thus, bleaching of these pulps does not produce chlorinated by-products.

Brightening of Recovered Fiber

Brightening of most recycled pulps is accomplished with either sodium hypochlorite or non-chlorine based chemicals such as hydrogen peroxide, sodium hydrosulfite or formamidine sulfonic acid (FAS) (Dence and Reeve 1996). Mills that do not use hypochlorite or other chlorine-containing chemicals for brightening are said to operate process chlorine free, or PCF.

Chloroform is produced as a by-product of brightening with hypochlorite. The generation of chloroform in recovered brightening stages using hypochlorite is similar in magnitude as that associated with hypochlorite bleaching of virgin pulps ranging between about 0.12 and 1.2 kg/air dry metric ton (ADMT) of pulp (Dence and Reeve 1996). A portion of this chloroform would be emitted in bleach plant vents and the remainder with bleach plant wastewater sent for treatment. Elimination of hypochlorite from the brightening system in favor of peroxide or other non-chlorine containing brightening agents would eliminate most or all generation of chloroform.

Carbon Monoxide is produced when hydrogen peroxide is used as a brightening agent. Conversion of hypochlorite brightening to peroxide brightening would be expected to result in increased industry emissions of carbon monoxide.

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