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Subject: Section 112(d)(6) Technology Review for Pulping and Papermaking Processes  
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From: Katie Hanks  
Thomas Holloway

To: John Bradfield  
Bill Schrock  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711

The purpose of this memorandum is to present the results of a review of available information on developments in practices, processes, and control technologies that apply to pulping and papermaking processes. This analysis is part of the U.S. Environmental Protection Agency's (EPA's) effort to review the national emission standards for hazardous air pollutants (NESHAP) for the Pulp and Paper Industry (40 CFR part 63, subpart S) in accordance with section 112(d)(6) of the Clean Air Act (CAA).

Section I of this memorandum provides background information on the requirements of section 112(d)(6) of the CAA, the pulp and paper production source category, and the requirements of the Pulp and Paper NESHAP. Section II discusses the review of information on developments in practices, processes, and control technologies that have occurred since the original development of this NESHAP. The specific processes mentioned in this memorandum include:

- Kraft pulping processes
- Soda pulping processes
- Semichemical pulping processes
- Sulfite pulping processes
- Non-wood pulping processes
- Mechanical pulping
- Secondary fiber pulping processes
- Papermaking processes

Separate memoranda present detailed technology reviews for kraft pulping process condensates and bleaching systems. (EPA 2011a, EPA 2011b)

## **I. Background**

### ***A. Requirements of Section 112(d)(6) of the CAA***

Section 112 of the CAA requires EPA to establish technology-based standards for sources of hazardous air pollutants (HAP). These technology-based standards are often referred to as maximum achievable control technology (MACT) standards. Section 112 also contains provisions requiring EPA to revisit these standards. Specifically, paragraph 112(d)(6) section states:

(6) REVIEW AND REVISION. – The Administrator shall review, and revise as necessary (taking into account developments in practices, processes, and control technologies), emission standards promulgated under this section no less often than every 8 years.

For the purpose of this technology review, a “development” was considered to be any of the following:

- Add-on control technology or other equipment that was not identified and considered during the development of the NESHAP;
- Improvements in add-on control technology or other equipment that were not identified and considered during NESHAP development that could result in significant additional HAP emissions reductions;
- Work practice or operational procedure that was not identified and considered during NESHAP development; and
- Process change or pollution prevention alternative that could be broadly applied that was not identified and considered during the development of the NESHAP.
- Improvements in work practices, operational procedures, process changes or pollution prevention alternatives

### ***B. Description of Source Category and NESHAP Requirements***

The pulp and paper production source category includes any facility engaged in the production of pulp and/or paper. This category includes, but is not limited to, integrated mills (where pulp alone, or pulp and paper, or paperboard are manufactured on-site), non-integrated mills (where either pulp or paper/paperboard are manufactured on-site, but not both), and secondary fiber mills (where waste paper is used as the primary raw material).

The processes used to convert wood into paper products include: wood preparation (debarking, chipping, and sizing of the wood material); pulping (chemical, mechanical, semichemical, or recycled paper pulping); chemical recovery (recovery of pulping chemicals in chemical and semichemical pulping); bleaching (chemically whitening/brightening the pulp); and papermaking (stock preparation, dewatering, pressing, drying, and finishing). A fully-integrated chemical pulp and paper mill would include all of these process areas.

The MACT standards for the pulp and paper production source category were developed in three parts:

- MACT I - regulates HAP emissions from the pulp production areas and bleaching operations at chemical pulp mills (kraft, sulfite, semichemical, and soda wood pulping processes) and the bleaching operations at pulp mills using mechanical, secondary fiber, and non-wood pulping;
- MACT II - regulates HAP emissions from the chemical recovery combustion areas of chemical pulp mills (kraft, sulfite, semichemical, and soda wood pulping processes); and
- MACT III - regulates HAP emissions from pulp and paper production areas of pulp mills using mechanical, secondary fiber, and non-wood pulping, and papermaking systems at all mills.

The MACT I and MACT III standards are contained in 40 CFR part 63, subpart S (NESHAP for the Pulp and Paper Industry), which was promulgated on April 15, 1998. As noted previously, the purpose of this memorandum is to present the results of a technology review for many sources subject to NESHAP subpart S.

The pulping and bleaching operations at kraft, soda, sulfite, and stand-alone semichemical pulp mills that are regulated by the MACT I rule include digesters, pulp washers, evaporators, turpentine recovery, steam stripper systems, liquor storage tanks, lime slaker vents, oxygen delignification systems, bleaching systems, wastewater treatment systems, and related equipment and processes. Bleaching operations at mechanical, secondary fiber, and non-wood pulp mills that are regulated by the MACT I rule include bleaching tower vents, storage tanks, washer vents, filtrate tank vents, scrubber outlets, and wastewater. Mills that mechanically pulp wood, pulp secondary fiber or non-wood fibers, and any mills that make paper, paperboard, or related products from pulp are entities covered by the MACT III rule. The processes evaluated under this standard include chip pre-steaming vessels, pulpers/repulpers, deinking operations at secondary fiber mills, and papermaking operations (e.g., forming, drying, vacuum pumps, storage tanks) at all mills.

As promulgated, the MACT I and III (subpart S) standards include emissions standards for pulping system vents, kraft pulping process condensates, and bleaching system vents. These standards also include several alternative emissions limits for each covered process that is designed to provide flexibility and promote and encourage the use of new technology, particularly combined air/water controls and pollution prevention technologies. Table 1 at the end of this memorandum presents an abbreviated summary of the subpart S standards. The control systems used by most mills to meet the subpart S emissions standards are as follows:

- Pulping system vents — thermal oxidizers, power boilers, lime kilns, and recovery furnaces.
- Pulping process condensates — steam strippers, biological wastewater treatment, and recycling to pulping equipment that is controlled by the standards.
- Bleaching system vents — caustic scrubbers (for chlorinated HAP other than chloroform) and process modifications to eliminate the use of chlorine and hypochlorite.

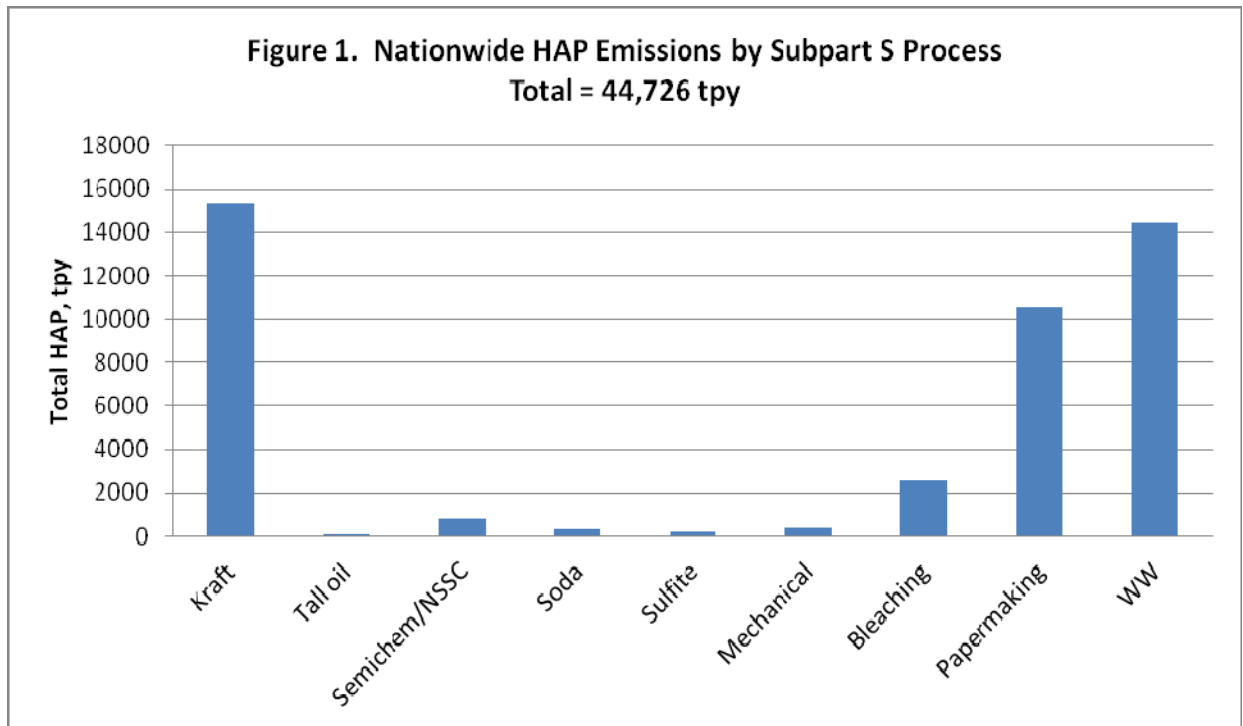
### *C. Estimated HAP Emissions*

Substantial HAP emission reductions have been achieved through implementation of subpart S for pulping and bleaching vents and kraft condensates. Nationwide baseline HAP emissions for the subpart S source category were estimated at 230,000 tons per year (tpy) prior to implementation of subpart S. (EPA1993) The EPA conducted an information collection request (ICR) in 2011 that requested updated emissions inventories from major source pulp and paper production facilities. Post-MACT nationwide emissions estimates based on responses to Part II of the pulp and paper ICR were 44,726 tpy. Methanol accounts for 86 percent of the total HAP emissions, while acetaldehyde accounts for 5 percent. Numerous other HAP account for the remaining emissions reported for subpart S equipment in Part II of the ICR. Table 2 at the end of this memorandum presents a list of the pollutants and their reported emissions for equipment in the subpart S source category. Figure 1 depicts the magnitude of subpart S emissions by process. Processes with the most emissions following MACT implementation are kraft pulping, wastewater, and papermaking. Bleaching emissions remain as well, but are not of the same magnitude as the aforementioned processes. Emissions from non-kraft pulping processes are very low relative to kraft pulping, in part because there are fewer of these processes nationwide, and because the emissions sources in these processes differ from kraft processes.

At the time of subpart S promulgation, it was concluded that wood yard operations, tall oil recovery systems, and pulping systems at mechanical, secondary fiber, and non-wood fiber pulping mills do not emit significant quantities of HAPs. (72 FR 18519, April 15, 1998) As clearly shown in Figure 1 for tall oil and mechanical pulping, this conclusion remains true today following MACT implementation. Wood yards do not appear in Figure 1 because no HAP data for wood yards were reported in the Part II subpart S inventory. Secondary fiber operations also are not shown separately on Figure 1 because they are often co-located with and integrated into other pulping or papermaking operations, and, therefore, secondary fiber emissions are embedded in the Figure 1 bars for other processes. There are no known major source non-wood mills (e.g., the only non-wood mill responding to the ICR was found to be a true area source). Consequently, the remainder of this memorandum focuses on chemical pulping processes and papermaking with limited additional discussion of the processes noted in this paragraph.

## **II. Developments in Practices, Processes, and Control Technologies**

The RACT/BACT/LAER Clearinghouse (RBLC) and responses to Part I of EPA's pulp and paper ICR were reviewed to determine if there have been developments in practices, processes, or control technologies for pulping and papermaking. In addition, we contacted states for details on BACT determinations made for papermaking processes. No new measures for reducing pulping HAP emissions were identified beyond the technologies used to comply with MACT for most equipment. A separate memorandum discusses the technology review for kraft condensates (wastewater), where a separate investigation was performed. The technology review for bleaching is also provided in a separate memorandum, though no new emissions reduction measures were identified.



#### ***A. RACT/BACT/LAER Clearinghouse***

The information found in our search of the RBLC is described and tabulated in a separate memorandum. (RTI 2011a) A few emissions reduction measures for pulping processes were identified in the RBLC. Pulping emissions of HAP, volatile organic compound (VOC), total reduced sulfur (TRS), and/or acetone at 12 kraft pulp mills were controlled by routing them to an incineration device, such as a boiler, lime kiln, recovery furnace, or thermal oxidizer. Pulping condensate VOC and TRS emissions in wastewater at two mills were controlled by biodegradation or good management practices. In each of these cases, the information obtained through the RBLC search did not represent any practices, processes, or control technologies not already identified and evaluated during the original MACT development. The findings of EPA's ICR relative to these controls are described below.

Controls other than those considered as HAP-reducing technologies during the original MACT development were also noted in the RBLC for some processes. Specifically, lime slaker particulate matter (PM) emissions at one mill were controlled by a wet scrubber. Tall oil recovery system VOC emissions at one mill were controlled by venting them to incineration-based control. Pulping VOC emissions were controlled at two mechanical pulp mills by using a regenerative thermal oxidizer (RTO) and at one mill by using existing fiber scrubbers/condensers. Non-HAP VOC (e.g., pinenes) are the predominant pollutants from tall oil recovery and mechanical pulping systems. TRS may also be important for tall oil recovery.

## B. Review of Pulp and Paper Part I Survey Data

### 1. Kraft pulping processes

Ninety-seven mills in the Part I data base perform kraft pulping which is a chemical pulping process that uses a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na<sub>2</sub>S) as the cooking liquor. Figure 2 is a general diagram of the kraft pulping process.

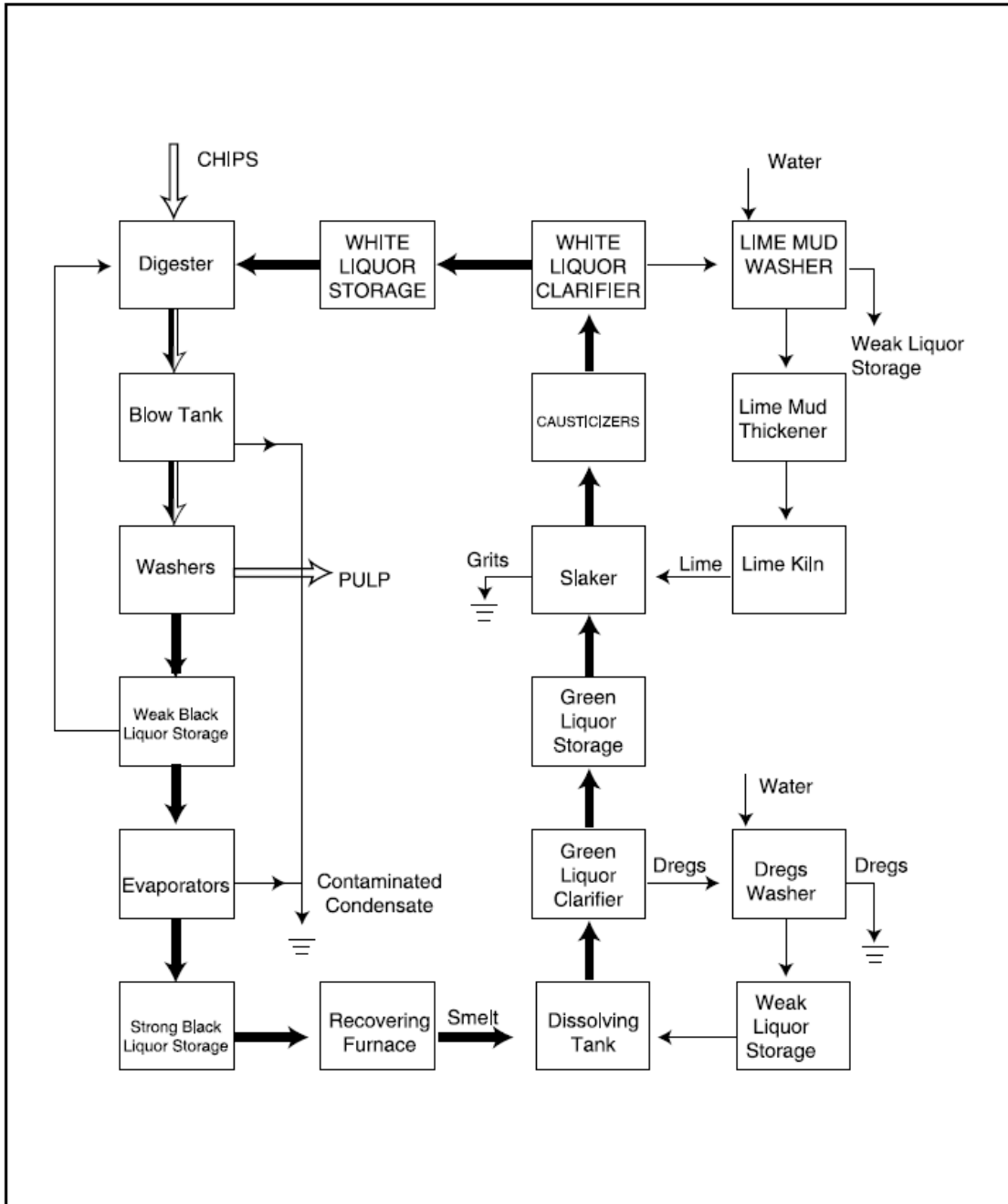


Figure 2. General Diagram of the Kraft Pulping Process (Smook 2002)

Kraft pulping emissions sources include the digester, washer, evaporator, black liquor storage, knotter, screen, oxygen delignification, steam stripper, causticizing, and turpentine production systems. Each of these systems is comprised of several pieces of process equipment and multiple vents. Vent gas collection systems are used to transport emissions to a control device. Subpart S defines the following collection systems:

*High volume, low concentration or HVLC system* means the collection of equipment including the pulp washing, knotter, screen, decker, and oxygen delignification systems, weak liquor storage tanks, and any other equipment serving the same function as those previously listed.

*Low volume, high concentration or LVHC system* means the collection of equipment including the digester, turpentine recovery, evaporator, steam stripper systems, and any other equipment serving the same function as those previously listed.

These collection systems are often referred to more generally as non-condensable gas (NCG) collection systems. The gas collection systems typically route the collected vent gases to a combustion unit such as a thermal oxidizer, lime kiln, recovery furnace, process heater, or boiler for incineration-based control (destruction) of HAP emissions.

Based on our review of the Part I survey data, it is apparent that the actual configuration of NCG systems is mill-specific, and configurations are not constrained by the equipment listings in the definitions of “HVLC system” and “LVHC system” above. For example, some vents from an evaporator system (technically part of the LVHC system definition) may be collected in the HVLC system; or some pulp washing system vents (technically part of the HVLC system definition) may be collected in the LVHC system. Some mills do not refer to their systems as “LVHC” or “HVLC” but simply refer to their NCG collection system. Stripper off gases (SOGs), which are technically part of the LVHC system by definition, are also referred to separately and often have their own collection system. Regardless of how the collection system is configured or referred to, the end result of incineration-based control is the same. In this memorandum, for simplicity, we will refer to LVHC, HVLC, NCG, and SOG collection systems as the “NCG system.”

The most common incineration-based controls reported in the Part I survey for NCG systems included lime kilns, power boilers, thermal oxidizers, and recovery furnaces. Some mills reported use of scrubbing in conjunction with incineration-based control. In some cases, white liquor scrubbers are used prior to incineration to remove TRS from the emissions stream to be incinerated (to prevent sulfur dioxide [SO<sub>2</sub>] emissions). In other cases, a scrubber may appear after incineration-based control (e.g., as the boiler or lime kiln’s control device; or as an SO<sub>2</sub> scrubber on a thermal oxidizer). A few mills reported use of scrubbers both before and after incineration-based control. In addition, 80 kraft mills reported use of backup controls for some portion of their NCG systems.

Digester systems. Continuous or batch digester systems are used for the chemical treatment of wood or non-wood fibers. Digester chip bins that pre-steam the wood chips may operate under high or low pressure and are considered part of the overall digester system if, as defined in subpart S, the steam used is not fresh steam. Several chip bins pre-steaming wood

chips were noted in the Part I survey responses as being routed through the NCG system for incineration-based control (e.g., in a lime kiln, boiler, recovery furnace, or thermal oxidizer).

Other components of the digester systems include associated flash tanks, blow tanks, blow heat recovery accumulators, relief gas condensers, prehydrolysis units preceding the pulp washing system, and related equipment. These components are routed to incineration-based control through the NCG system, consistent with the control requirements under subpart S.

The practices, processes, and controls reported in the Part I survey responses for digester systems were consistent with those evaluated during MACT development. No new developments were identified.

Pulp washing systems. Pulp washing systems are part of the HVLC system and include all equipment used to wash pulp and separate spent cooking chemicals following the digester system and prior to the bleaching system, oxygen delignification system, or papermaking system (at unbleached mills). The pulp washing system equipment includes vacuum drum washers, diffusion washers, rotary pressure washers, horizontal belt filters, intermediate stock chests, and their associated vacuum pumps, filtrate tanks, foam breakers or tanks, and related equipment.

Controls reported in the Part I survey for kraft pulp washing included incineration-based controls typical of NCG systems. Process improvements noted by some mills included use of clean condensates (e.g., stripped condensates) or fresh water on the last stage of pulp washing. These types of process improvements and controls were previously identified and evaluated during the original MACT development.

As part of the HVLC system, pulp washing system vent gases are eligible for use as emissions averaging debits under the clean condensate alternative (CCA). As discussed in a separate memorandum, 38 mills used the CCA as part of their MACT compliance strategy. (EPA 2011c)

No new developments in practices, processes, or controls were observed for pulp washing systems.

Evaporator systems. Evaporator systems include equipment associated with increasing the solids content and/or concentrating spent cooking liquor from the pulp washing system. Pre-evaporators, multi-effect evaporators, concentrators, and vacuum systems, as well as associated condensers, hotwells, and condensate streams, and similar equipment are all part of the evaporator system.

Evaporation systems are part of the LVHC system defined in subpart S. Controls reported in the Part I survey for evaporator systems included NCG collection and incineration-based control. Some mills reported use of a scrubber-incineration control configuration (as also noted above for other equipment routed through the NCG system). No process controls specific to evaporator systems were reported.



No new developments in practices, processes, or controls were revealed in the Part I survey responses for evaporator systems.

Knotter and screen systems. Knotters remove knots, oversized material, or pieces of uncooked wood from the pulp slurry after the digester system and prior to the pulp washing system. The knotter system equipment includes the knotter, knot drainer tanks, ancillary tanks, and related equipment. Screens remove oversized particles from the pulp slurry prior to washed stock storage for bleaching or papermaking. Knotter and screen systems may be combined such that there is no vent in between systems.

The kraft pulping vent gas emission limits apply for all knotters and screens at new sources, and existing knotters and screens above certain total HAP levels (0.1 pounds [lb] of total HAP per ton of oven dried pulp [ODP] for knotters; 0.2 lb/ton ODP for screens; and 0.3 lb/ton ODP for knotters and screens). According to the Part I survey results, many knotters and screens are not vented, or a fugitive emission sources vented into a building. Vent gases for other knotters and screens are collected in the NCG system and incinerated.

No new developments in practices, processes, or controls were observed for knotters and screens.

Deckers. Deckers are used to thicken the pulp slurry or reduce its liquid content after the pulp washing system and prior to high-density pulp storage. The decker system includes decker vents, filtrate tanks, associated vacuum pumps, and related equipment. The kraft pulping vent gas emission limits apply for all new deckers and existing deckers using any process water other than fresh water or paper machine white water, or that use any process water with a total HAP concentration (measured as methanol) greater than 400 parts per million by weight (ppmw).

The Part I survey results indicated that most deckers are either uncontrolled (e.g., operating with fresh or white water) or are routed to the NCG system for incineration, consistent with the requirements of subpart S. A couple of mills noted, in general, that their foul condensate collection practices reduce emissions associated with process water (and as a result emissions from equipment using process water would be reduced, including the decker).

No new developments in practices, processes, or controls were observed for deckers.

Liquor storage. Spent pulping liquor is generated when cooking liquor is separated from the pulp during washing. Spent liquor contains dissolved organic wood materials and residual cooking compounds. After concentration in the evaporator system, this spent liquor (e.g., kraft black liquor) is a valuable fuel that is burned in the chemical recovery furnace. In addition to producing steam, the recovery furnace is where the process of reclaiming the residual inorganic cooking compounds begins. Kraft recovery furnaces are subject to a different MACT standard (subpart MM) and are not discussed further in this memorandum.

Spent liquor storage consists of various tanks (or, in rare cases, liquor ponds). Strong liquor storage tanks contain liquor that has been concentrated (through evaporation) in preparation for combustion or oxidation in the recovery process. Weak liquor storage tanks

(other than washer filtrate tanks) contain spent liquor recovered from the pulping process prior to the evaporator system. Weak liquor storage tanks are considered part of the HVLC system and are subject to the pulping vent gas standards for new kraft pulping lines. Strong (or heavy) liquor storage tanks are not subject to the pulping vent gas limits.

Most liquor tanks were reported as fugitive, vented into a building, or otherwise uncontrolled. Some weak, strong, and intermediate liquor tanks were reported as being vented to the NCG system for incineration control. One mill reported used of black liquor temperature control (to minimize flashing) but did not indicate how the temperature control was achieved. No other process changes specific to liquor storage HAP emissions were noted. Ten kraft mills reported use of liquor ponds, most likely temporary emergency storage areas used to capture spills or leaks, which can be inferred since these same ten kraft mills also reported use of a series of spent liquor storage tanks. Liquor ponds are fugitive emissions sources.

In sum, no new developments in practices, processes, or controls beyond NCG collection and incineration control were identified for liquor storage.

Oxygen delignification. Oxygen delignification is subject to the kraft pulping vent gas standards for new and existing pulping lines. Oxygen delignification uses oxygen to remove lignin from pulp after high-density stock storage and prior to the bleaching system. The oxygen delignification system equipment includes the blow tank, washers, filtrate tanks, any interstage pulp storage tanks, and any related equipment.

Based on review of the Part I survey results, most oxygen delignification systems are vented through the NCG system to incineration-based control. A few oxygen delignification systems are not vented, some are included as a debit generated source under the CCA, and a few are subject to site-specific MACT provisions or equivalency by permit.

No process controls were noted. No new developments in practices, processes, or controls were identified for oxygen delignification.

Condensate strippers. Condensate strippers are most commonly steam strippers. Steam stripper systems contain a column used to remove compounds from wastewater or condensates using steam, stripper feed tanks, condensers, or heat exchangers, and (if present at the mill) equipment associated with a methanol rectification process including rectifiers, condensers, decanters, storage tanks, and related equipment. Steam stripper system vents are commonly controlled through collection and incineration of the SOG.

No new developments in practices, processes, or controls beyond SOG collection and incineration control were identified for condensate strippers. However, as discussed in a separate memorandum pertaining to kraft condensates, the HAP removal efficiency of steam strippers is expected to have improved since promulgation of subpart S. (EPA 2011a)

Causticizing. In the kraft pulping process, smelt exiting from the recovery furnace is causticized to remove impurities left over from the furnace and to convert sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) into active NaOH. The causticizing procedure begins with the mixing of smelt with

“weak” liquor to form green liquor, named for its characteristic color. Contaminant solids, called dregs, are removed from the green liquor, which is mixed with lime (CaO). After the lime mixing step, the mixture, now called white liquor due to its new coloring, is processed to remove a layer of lime mud (CaCO<sub>3</sub>) that has precipitated. The primary chemicals recovered are caustic (NaOH) and Na<sub>2</sub>S. The remaining white liquor is then used in the pulp cooking process. The lime mud is treated to regenerate lime in the lime kiln calcining process. (EPA 2002)

Figure 2 shows the kraft pulping process with chemical recovery, including the causticizing loop. The principle equipment in the causticizing loop include:

- Equipment handling green liquor (e.g., green liquor clarifiers, green liquor storage tanks, dregs washers)
- Slaker (and associated slaker grits handling equipment)
- Causticizer tanks
- White liquor clarifier and storage tanks
- Lime mud washer, precoat filter (thickener), and associated weak wash tanks

Lime kilns are covered under a separate MACT standard (i.e., subpart MM) for chemical recovery combustion sources.

According to the Part I data base, no add-on controls are used for green liquor processing. Green liquor tanks were mostly uncontrolled fixed roof tanks, though there are a few open tanks (some of which are in a building). Several mills reported that their green liquor processing equipment is a source of fugitive emissions (i.e., not vented through a conveyance). Process techniques that may reduce HAP were reported, including use of stripped condensates and makeup water derived from freshwater.

Particulate matter is generated from the strong reaction of the lime with green liquor in the slaker, which produces some steam. The steam carries PM with it as it is released out the vent. Slakers operate with some form of water spray scrubbing designed for PM control. Based on emission unit descriptions, it appears that some slakers and causticizers may vent through the same scrubber. Slakers (and causticizers) at one mill were reported to be vented to a scrubber and lime kiln, while the slaker at another mill was reported to vent to the LVHC collection system, where emissions are destroyed by a lime kiln. The effectiveness of slaker scrubbers at reducing HAP is limited. General process techniques reported that may reduce HAP from slakers and causticizers include use of stripped condensates and makeup water derived from freshwater.

Most lime mud handling equipment is uncontrolled. However, dust collectors (mainly baghouses) were reported for some lime mud handling systems. One facility uses the lime kiln electrostatic precipitator (ESP) for PM control. Two facilities use the lime kiln wet scrubber for particulate control. Although no add-on controls specific to HAP are used for lime mud processing, use of fresh water or clean process water (i.e., water that is not contaminated with untreated condensates) is a process control measure in use by many facilities.

Add-on controls for weak wash handling are non-existent, with one exception. One weak wash storage tank was reported to be routed to HVLC and incinerated in a boiler. Of the weak

wash handling units that were reported, most of the tanks had a fixed roof. No process controls (beyond those mentioned above in general) were reported.

Most causticizers, white liquor clarifiers, and white liquor tanks are uncontrolled. Most tanks are fixed roof tanks, though some have an open roof (often located in a building). Some white liquor processing equipment was reported as a fugitive emission source. A few were reported to have a wet scrubber or mist eliminator, but it is not clear whether these scrubbers would have any effect on HAP emissions. In some cases, the slaker scrubber is used. General process techniques reported that may reduce HAP include use of stripped condensates and makeup water derived from freshwater.

Miscellaneous causticizing equipment includes equipment that could not be easily characterized based on the emission unit description provided in the ICR (or did not fit in the green liquor, lime mud, slaker, or white liquor groupings). Nearly all of this equipment is uncontrolled with the following three exceptions:

- A “Causticizer Receiver Tank” that operates with wet scrubber control
- A “MACT I Phase I Tank” that operates with scrubber and lime kiln control
- A “Recovery Accumulator” that is routed through the LVHC system for thermal oxidizer control

These equipment are believed to be unique and specific to the mill where they operate, and, therefore, are not considered further in the technology review.

In general, causticizing equipment does not operate with HAP-reducing add-on controls (with the exception of a couple of random causticizing units tied into an NCG system). Process techniques reported that may reduce HAP emissions include use of stripped condensates as causticizing equipment makeup water or makeup water derived from freshwater. Use of process liquids including evaporator or recycled condensates was reported by some mills. Recycling of kraft condensates is one compliance option available to facilities that must meet the requirements of 40 CFR 63.446. However, most mills reporting use of condensates often reported use of such condensates along with fresh water as makeup to the causticizing system. Given the site-specific nature of condensate recycle practices (i.e., the extent to which treated vs. untreated condensates are reused), the lack of information on water flow rates and excess wastewater treatment plant capacity, and issues of fresh water availability, it would be extremely difficult to determine emissions reductions, costs, and impacts associated with changes to causticizing makeup water. As noted above, kraft mills are already subject to the subpart S kraft condensate standards, which require condensates to either be treated or recycled to process equipment subject to the pulping vent gas standards. Thus, reuse of contaminated condensates in causticizing equipment not subject to the vent gas standards is minimized by the existing kraft condensate standards. This is evidenced by the fact that post-MACT nationwide emissions from causticizing are low compared to other kraft pulping processes. Changes to the causticizing system were not explored further as part of the technology review for these reasons.

Turpentine production. Turpentine is often recovered as a byproduct from the digester gases at kraft pulp mills. Approximately 80 mills reported production of turpentine in response to the Part I survey. The turpentine recovery system includes condensers, decanters, storage tanks, and related equipment. Turpentine recovery is part of the LVHC system at kraft pulp mills.

No new developments in practices, processes, or controls beyond NCG collection and incineration were identified for turpentine recovery.

## 2. Soda pulping processes

Soda pulping is a chemical pulping process that uses NaOH as the active chemical in the cooking liquor. As shown in Table 1, LVHC system equipment at existing soda mills (digesters, evaporators, and steam strippers) is subject to the pulping vent gas standards in subpart S. In addition, the pulp washing system at new soda mills is subject to the pulping vent gas standards in subpart S. One soda pulping mill operates in the U.S. This mill operates a steam stripper to reduce emissions associated with condensates, and routes all affected emission points including washers and several liquor storage tanks to its NCG system and a thermal oxidizer control.

No new practices, processes, or controls were identified for soda pulping.

## 3. Semi-chemical pulping processes

As defined in subpart S, semi-chemical pulping means a pulping process that combines both chemical and mechanical pulping processes. The semi-chemical pulping process produces intermediate pulp yields ranging from 55 to 90 percent.

The major process difference between chemical pulping and semi-chemical pulping is that semi-chemical pulping uses lower temperatures, more dilute cooking liquor or shorter cooking times, and mechanical disintegration for fiber separation. There are two types of semi-chemical pulping processes currently in use—the neutral sulfite semi-chemical (NSSC) pulping process and the nonsulfur semi-chemical pulping process. The digestion step in the NSSC pulping process consists of heating pulp in sodium sulfite ( $\text{Na}_2\text{SO}_3$ ) and  $\text{Na}_2\text{CO}_3$ . The digestion step in nonsulfur semi-chemical pulping consists of heating pulp in  $\text{Na}_2\text{CO}_3$  alone or with NaOH.

A total of eight stand-alone semi-chemical pulp mills were reported in the Part I survey (two NSSC mills and six nonsulfur semi-chemical mills). This is a declining segment of the subpart S category; there were 32 semi-chemical mills in operation at rule promulgation. Secondary fiber pulps are now used in many of the same products as virgin semi-chemical pulp. Semi-chemical pulping is often combined with secondary fiber pulp processing. Since secondary fiber pulping is essentially a recycle operation (and not a chemical pulping process), we considered mills that produce only semi-chemical and secondary fiber pulps to be stand-alone semi-chemical pulping operations.

The subpart S pulping vent gas standards for semi-chemical mills apply to the LVHC system at existing sources and the LVHC system and pulp washing system at new sources. Emissions from these systems are to be enclosed, vented to a closed-vent system, and routed to a control device that either (1) reduces total HAP emissions by at least 98 percent; (2) reduces total HAP at the thermal oxidizer outlet to 20 ppmv or less; (3) reduces total HAP emissions using a thermal oxidizer operating at a temperature  $>1600^\circ\text{F}$  and a residence time  $>0.75$  seconds; or (4) reduces total HAP emissions using a boiler, lime kiln, or recovery furnace.

Based on information in the Part I database, all semi-chemical mills are equipped with some type of system for collecting and venting NCGs. Most mills vent the collected emissions to boilers, although a couple of mills vent the emissions to lime kilns. One mill uses a combination of a condenser and packed-bed scrubber to meet the 98 percent limit. We identified no new practices, processes, or controls for pulping processes at semi-chemical mills.

#### 4. Sulfite pulping processes

The sulfite pulping process relies on acid solutions of sulfurous acid ( $\text{H}_2\text{SO}_3$ ) and bisulfite ion ( $\text{HSO}_3^-$ ) as the cooking liquor. The bisulfate ion enters the process as a compound of the form  $\text{M}(\text{HSO}_3^-)$ , where the “M” may be calcium (Ca), ammonia ( $\text{NH}_3$ ), sodium (Na), or magnesium (Mg). Six mills reported sulfite pulping processes in response to the Part I survey. Three mills perform  $\text{NH}_3$ -based sulfite, two perform Ca-based sulfite, and one mill is co-located with kraft pulping and performs Na-based sulfite pulping. There are no longer any Mg-based sulfite mills. Sulfite pulping is a declining segment of the subpart S category; there were 16 sulfite mills in operation at rule promulgation.

The subpart S pulping vent gas standards for sulfite mills apply for digester, evaporator, and washer vent gases at existing sources. At new sources, the vent gas standards also apply for strong and weak liquor storage tanks, and acid condensate storage tanks. Acid condensate storage tanks store cooking acid following the  $\text{SO}_2$  gas fortification process used to generate  $\text{H}_2\text{SO}_3$ . Different numerical vent gas emission limits apply for Ca- and Na-based sulfite than for  $\text{NH}_3$  or Mg-based sulfite.

The HAP emissions at the Ca-based and  $\text{NH}_3$ -based sulfite mills are typically collected and routed through a scrubber system. The HAP emissions from equipment at the co-located kraft and Na-based sulfite mill are controlled through the kraft LVHC system. No new practices, processes, or controls were identified for sulfite mills.

#### 5. Pulp storage

All types of mills operate tanks, high density storage, stock chests, etc. to store pulp at various points along the pulp production line, prior to bleaching, or prior to papermaking. Several pulp storage tanks are either not vented, fugitive sources, or vented inside a building. Very few controls were noted for pulp storage in the Part I responses, with the exception of a few storage tanks that are connected with the mill’s NCG system (e.g., likely because they are part of a larger system with emission limits under subpart S). It was unclear from the descriptions provided in survey responses if the pulp storage may have been part of another system (e.g., some mills reported pulp storage for equipment that is part of the digester or washer system). No new process changes were noted for pulp storage.

#### 6. Papermaking

Papermaking includes equipment used to convert pulp into paper, paperboard, or market pulp, including the stock storage and preparation systems, paper or paperboard machines, paper

machine white water system, broke recovery systems, and the systems involved in calendering, drying, on-machine coating, slitting, winding, and cutting.

EPA previously (during original rule development) evaluated two undemonstrated control measures that could potentially reduce HAP emissions from papermaking: (1) removal of HAPs from the pulp stock and white water before the papermaking system (e.g., with a white water steam stripper); and (2) control of papermaking system vent streams through vent gas collection and incineration. Analysis of these control options concluded that there are no demonstrated methods for removing HAPs from the pulp stock or white water and that applying HAP control to the vent streams of papermaking systems is not cost-effective (Air Docket A-95-31, IV-B-8 [ERG 1997a]). Technical challenges noted with these two control options included fiber clogging of the steam stripper columns and heat exchangers, and the extremely high air flow rates from paper machines to be treated with incineration controls.

The EPA also investigated the use of HAP-containing additives in papermaking systems, the magnitude of HAP emissions resulting from the use of papermaking system additives, and the viability of a MACT standard based on additive substitution. It was concluded that additives did not contribute significantly to HAP emissions from the paper industry, with only 20 percent of the HAP additive content emitted to air, while the remaining 80 percent remained in the paper product or white water. The industry-wide total annual HAP emissions attributable to additives were estimated to be around 50 tpy, and were considered negligible in comparison to the industry pre-MACT baseline emissions of over 200,000 tpy of total HAPs. EPA also noted that papermaking chemical and additive suppliers are continually working to reduce the HAP content of additives, but that it was not clear from available information that substitution options are technically feasible for all products. Therefore, EPA concluded that a standard for papermaking systems based on low-HAP additive substitution was not warranted at the time of promulgation in 1998. (72 FR 18525-18526, April 15, 1998 and Air Docket A-95-31, Item IV-B-6 [ERG 1997b]).

As part of the current technology review, the Part I ICR data along with BACT determinations for papermaking were examined to determine if there have been developments in practices, processes, or controls applicable to papermaking systems since subpart S promulgation in 1998. (RTI 2011b) The only available measures for reducing papermaking HAP emissions include process changes or work practices (e.g., practices relating to VOC in papermaking additives). Add-on controls for HAP emissions have not been put into practice and remain undemonstrated.

### III. References

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**Table 1. Summary of MACT I and III (Subpart S) Standards**

Source limit details	Typical source control systems	Gaseous organic HAP standard
<p><u>Kraft pulping vent gases:</u> Existing sources: LVHC system<sup>1</sup>; knotter or screen (above HAP cutoffs), pulp washing, decker (using contaminated water), and O<sub>2</sub> delignification.</p> <p>New sources: Same as existing, except applies for <u>all</u> knotters, screens, and deckers plus weak liquor storage tanks.</p>	<p>Route through a closed vent collection system to a boiler, lime kiln, recovery furnace, or thermal oxidizer</p>	<p>(1) Reduce total HAP emissions by <math>\geq 98</math> wt%; or</p> <p>(2) Reduce total HAP concentration at the outlet of thermal oxidizer to <math>\leq 20</math> ppmv @ 10% O<sub>2</sub> (dry basis); or</p> <p>(3) Reduce total HAP emissions using a thermal oxidizer operating <math>\geq 1600^{\circ}\text{F}</math> and <math>\geq 0.75</math> sec residence time; or</p> <p>(4) Use a boiler, LK, or RF in which the HAP gas stream is introduced with the primary fuel into the flame zone; or</p> <p>(5) Use a boiler or RF with a heat input capacity <math>\geq 150</math> MMBtu/hr (44 MW) in which the HAP gas stream is introduced with the combustion air.</p>
<p><u>Soda or semichemical pulping vent gases:</u> Existing sources: LVHC system<sup>1</sup></p> <p>New sources: Same as existing, plus pulp washing system.</p>	<p>Route through a closed vent collection system to a boiler, lime kiln, recovery furnace, or thermal oxidizer</p>	<p>(1) Reduce total HAP emissions by <math>\geq 98</math> wt%; or</p> <p>(2) Reduce total HAP concentration at the outlet of thermal oxidizer to <math>\leq 20</math> ppmv @ 10% O<sub>2</sub> (dry basis); or</p> <p>(3) Reduce total HAP emissions using a thermal oxidizer operating <math>\geq 1600^{\circ}\text{F}</math> and <math>\geq 0.75</math> secs residence time; or</p> <p>(4) Use a boiler, LK, or RF in which the HAP gas stream is introduced with the primary fuel into the flame zone; or</p> <p>(5) Use a boiler or RF with a heat input capacity <math>\geq 150</math> MMBtu/hr (44 MW) in which the HAP gas stream is introduced with the combustion air.</p>
<p><u>Sulfite pulping vent gases:</u> Existing sources: Digester vent, evaporator vent, and pulp washing.</p> <p>New sources: Same as existing, plus strong and weak liquor storage tanks, and acid condensate storage tanks.</p>	<p>Route through a closed vent collection system to a scrubber or other control device (emission limits apply to combined emissions from vents, control device wastewater, and condensates)</p>	<p>(1a) <u>Ca- or Na-based:</u> Emit total HAP (as methanol) <math>\leq 0.89</math> lb/ton ODP, or</p> <p>(1b) <u>Ca- or Na-based:</u> Reduce total HAP (as methanol) by <math>\geq 92\%</math>;</p> <p>(2a) <u>NH<sub>3</sub>- or Mg-based:</u> Emit total HAP (as methanol) <math>\leq 2.2</math> lb/ton ODP, or</p> <p>(2b) <u>NH<sub>3</sub>- or Mg-based:</u> Reduce total HAP (as methanol) by <math>\geq 87\%</math>.</p>

Source limit details	Typical source control systems	Gaseous organic HAP standard
<p><u>New and existing bleaching vent gases</u>: Chlorine bleaching systems, kraft/sulfite/soda bleaching with any chlorinated compounds, and mechanical/secondary fiber/non-wood bleaching with ClO<sub>2</sub>.</p>	<p>Route through a closed vent collection system to a caustic scrubber or similar device</p>	(1) Reduce total chlorinated HAP (except chloroform) limit: $\geq 99$ wt%, or
		(2) Meet $\leq 10$ ppmv of total chlorinated HAP (except chloroform) at control device outlet, or
		(3) Meet $\leq 0.002$ lb total chlorinated HAP (except chloroform)/ton ODP at control device outlet.
		(4) Work practice for chloroform - either meet effluent guidelines or use no hypochlorite or chlorine for bleaching.
<p>Kraft pulping process condensates (process liquids) from digester, turpentine recovery, evaporator, LVHC system<sup>1</sup>, and HVLC system<sup>2</sup> (some exceptions)</p>	<p>Route through a closed vent collection systems to pulping equipment</p>	(1) Reduce total HAP emissions by $\geq 98$ wt%; or
		(2) Reduce total HAP concentration at the outlet of thermal oxidizer to $\leq 20$ ppmv @ 10% O <sub>2</sub> (dry basis); or
		(3) Reduce total HAP emissions using a thermal oxidizer operating $\geq 1600^\circ\text{F}$ and $\geq 0.75$ secs residence time; or
		(4) Use a boiler, LK, or RF in which the HAP gas stream is introduced with the primary fuel into the flame zone; or
		(5) Use a boiler or RF with a heat input capacity $\geq 150$ MMBtu/hr (44 MW) in which the HAP gas stream is introduced with the combustion air.
	<p>Route to biological treatment/steam stripper or other control device</p>	(1) Reduce total HAP $\geq 92$ wt%; or
		(2a) For mills without bleaching, remove $\geq 6.6$ lb total HAP/ton ODP, or
		(2b) For mills without bleaching, meet $\leq 210$ ppmw total HAP at control device outlet; or
		(3a) For mills with bleaching, remove $\geq 10.2$ lb total HAP/ton ODP, or
		(3b) For mills with bleaching, meet $\leq 330$ ppmw total HAP at control device outlet.
<p>Clean condensate alternative (CCA) is an emissions averaging approach to offset emissions from certain existing kraft pulping sources.</p>	<p>Install and operate clean condensate alternative technology.</p>	<p>Emissions reductions from CCA <math>\geq</math> emissions reductions achieved through kraft pulping HVLC system standards</p>

<sup>1</sup>The LVHC system includes digester, turpentine recovery, evaporator, and steam strippers.

<sup>2</sup>The HVLC system includes pulp washing, knotter, screen, decker, O<sub>2</sub> delignification, weak liquor storage tanks.

**Table 2. Nationwide HAP Emissions from the Subpart S Source Category  
Reported in Part II of the 2011 ICR**

<b>HAP Category Name</b>	<b>Nationwide HAP emissions, tpy</b>
Methanol	38,650
Acetaldehyde	2,029
Cresol/Cresylic Acid (Mixed Isomers)	758
Phenol	454
Chloroform	356
Formaldehyde	274
Hydrochloric Acid	259
Biphenyl	218
Hexachloroethane	207
Xylenes (Mixed Isomers)	137
Propionaldehyde	135
1,2,4-Trichlorobenzene	129
Methylene Chloride (Dichloromethane)	120
Acrolein	101
Carbon Disulfide	90
Cumene	83
Toluene	82
Styrene	77
Tetrachloroethylene (Perchloroethylene)	75
Methyl Isobutyl Ketone (Hexone)	61
Acetophenone	60
Hexane	56
Carbon Tetrachloride	40
Trichloroethylene	37
Benzene (Including Benzene From Gasoline)	25
Naphthalene	24
Chlorine	24
1,1,2-Trichloroethane	23
Methyl Chloroform (1,1,1-Trichloroethane)	22
Ethylbenzene	18
Vinyl Acetate	16
Chlorobenzene	15
Methyl Chloride (Chloromethane)	14
Hexachlorocyclopentadiene	10
Vinylidene Chloride (1,1-Dichloroethylene)	8
Glycol Ethers	7
Acetonitrile	5
Ethylene Dichloride (1,2-Dichloroethane)	4
Vinyl Chloride	4
Triethylamine	3
Carbonyl Sulfide	3
Acrylonitrile	3
Chloroacetic Acid	2
Pentachlorophenol	1
Ethylene Glycol	0.8
Diethanolamine	0.8

HAP Category Name	Nationwide HAP emissions, tpy
Cyanide Compounds	0.7
1,3-Butadiene	0.5
2,4,5-Trichlorophenol	0.4
Methyl Bromide (Bromomethane)	0.3
Nickel Compounds	0.2
Acrylamide	0.2
Ethylene Dibromide (Dibromoethane)	0.1
Nitrobenzene	0.1
Antimony Compounds	0.1
Lead Compounds	0.1
Propylene Dichloride (1,2-Dichloropropane)	0.1
2-Nitropropane	0.05
Toluene-2,4-Diamine	0.02
Methyl Iodide (Iodomethane)	0.02
Chromium Compounds	0.02
Ethylidene Dichloride (1,1-Dichloroethane)	0.01
Bromoform	0.01
Cadmium Compounds	0.01
Beryllium Compounds	0.01
2,4,6-Trichlorophenol	0.01
Polycyclic Organic Matter as 15-PAH	0.01
Manganese Compounds	0.01
Catechol	0.01
N,N-Dimethylaniline	0.005
Mercury Compounds	0.004
Arsenic Compounds(Inorganic Including Arsine)	0.004
Selenium Compounds	0.004
Dibutyl Phthalate	0.003
1,4-Dichlorobenzene	0.003
Chlorobenzilate	0.002
Cobalt Compounds	0.002
Bis(2-Ethylhexyl)Phthalate (Dehp)	0.001
Polycyclic Organic Matter as non-15 PAH	0.001
Polycyclic Organic Matter as 7-PAH	0.001
1,1,2,2-Tetrachloroethane	0.001
Ethylene Oxide	0.0003
Aniline	0.00001
<b>Total</b>	<b>44,726</b>