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Washington State Air Toxic Sources and Emission Estimation Methods

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Washington State Air Toxic Sources and Emission Estimation Methods

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Introduction

Purpose

The purpose of the original document, *Air Toxics Emissions Estimation Methods Evaluation*, was to establish sound methods for estimating air toxic emissions. These methods would be used to develop emission inventories to support rule development, the operating permit and registration programs, and other studies. In this revision, the purpose expands to include process descriptions, variables, current control equipment, Reasonable Available Control Technology (RACT) and Maximum Available Control Technology (MACT) standards. The report should be looked at as a starting point for air toxics information, and the references at the end of each chapter can be used for more detailed information. While the original document also touched on criteria pollutants, this document will focus its efforts on air toxics, specifically those listed in Chapter 173-460 WAC.

Process

As a starting point, engineers and planners evaluated the list of source categories addressed in the first publication and surveyed local air authorities and other Ecology engineers for input on revisions. The result of this evaluation was to remove certain categories from the list and add others. Those categories that were removed are grain elevators, alfalfa cubers, cattle feedlots, and biogenic emissions. These categories were removed because they emitted little or no air toxics in Washington. Those categories that were added include sulfite pulp mills and secondary aluminum mills. The original publication was reviewed and new methods of determining emissions were researched.

For this revision, only some source categories were revised and updated. Others were not revised because there was no new information available. Those that were revised and updated are aluminum mills (primary and secondary), boilers, chemical pulp mills (Kraft and sulfite), and dry cleaners.

How to Use this Document

Each source category is broken up into two major components: *Description of Process* and *Methods of Determining Emissions*. These two components are addressed for each process within the source category.

Description of Process includes a short general description of the process. This is meant to be a starting point. We encourage you to look in some of the references included in each section for more information.

Methods of Determining Emissions includes:

- the most common toxic emissions;

- an overview of what emission factors are available and where or if there are no emission factors, what is the best method for emissions estimation;
- variables of the process (what affects the emissions?);
- control equipment available; and
- RACT or MACT analysis completed or planned in the near future.

We recommend that you refer to the emission factor sources referenced at the end of each chapter to see if the factors are applicable to your needs. Emissions factors are not specifically listed in this document due to frequent changes in emission factors. The recommended document or reference should be used to get the most current emission factors.

Where possible, emissions estimates should be based on source-specific data. Since this is not always possible, this publication can assist you in determining if more general emission factors are available and what the best methods of emissions estimation are. Care should be taken to check emission factor references. Many of the emission factors available for estimating emissions are based on very limited data. In discussing emissions estimation methods, this report brings out assumptions in currently available emission factors, so judgments can be made about their applicability to individual sources. The end use will often dictate the acceptability of given methods.

An expertise list is attached with contact names and phone numbers for each source category. You are encouraged to contact these people with questions and to get updates to source categories in this report.

Washington State Department of Ecology documents can be requested by calling the Publications Distribution Center at (360) 407-7472. For more information or if you have special needs, please contact the Air Quality Program at (360) 407-6830.

Future Recommendations

We recommend that this document be updated periodically. Sections should be revised or replaced when needed, as is done with AP-42. The Air Quality Program should check and update sections on a regular basis. Source categories should be accessed annually to see if this is necessary.

Some ideas were considered for inclusion in appendices, but could not be accomplished with current resources. These ideas should be considered for inclusion in future updates. They include development of appendices or databases with completed health risk assessments (including source, date, contact person), list of applicable regulations for each source category, list of Washington source tests, and a list of permitting issues that have occurred (including the name and phone number of engineer).

Aluminum Production

Aluminum is produced by aluminum ore refining and reduction (*primary production*) or from recycling aluminum (*secondary production*). The U.S. aluminum industry is the world's largest, producing 7.5 million tons in 1996. Aluminum production in the U.S is approximately 52% primary aluminum and 48% secondary aluminum. In 1996, 62.8 billion aluminum cans were recycled in the U.S. The Pacific Northwest aluminum facilities carry 38.6% of the U.S. primary aluminum capacity and have the ability to produce 1.8 million tons of aluminum. The largest markets for aluminum are transportation, packaging (beverage cans), and infrastructure. (Aluminum Association, Inc., 1997)

In Washington, primary aluminum production facilities are one of the largest producers of toxic emissions. There are currently seven primary aluminum production facilities and one secondary aluminum production facility in Washington. The largest toxic emissions from primary aluminum production are from fluorides and polycyclic organic matter. The largest toxic emissions from secondary aluminum production are chlorine and hydrogen chloride.

Primary Aluminum

Primary aluminum production encompasses two processes:
I. Refining: grinding and handling of the bauxite ore
II. Reduction: aluminum is removed from crystalline alumina

The refining process produces mainly particulate emissions and controls are used to recover much of this valuable dust. Since there are no refining processes in Washington and emissions are low and mostly comprised of particulate matter, the refining process will not be included in this report. If needed, more information can be found in *AP-42*[1].

The rest of this section will focus on the reduction process.

Description of Process

The aluminum enters the reduction process as crystalline alumina (Al_2O_3) from the refining process. To produce aluminum metal the alumina is electrolytically reduced using the Hall-Heroult Process.

Reduction occurs by reacting the alumina with carbon, as in the following reaction:

$$2\ Al_20_3 + 3\ C \rightarrow 4\ Al + 3\ CO_2$$

The carbon is in the form of an anode (negatively charged) which is continuously depleted. The *pots* (shallow rectangular steel shells) are also lined with carbon, which is positively charged and

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[1] U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, October 1997, Document No. AP-42.

acts as a cathode where the molten aluminum is deposited. Molten cryolite is used as the electrolyte and also as a solvent.

The molten aluminum is tapped from the cathode every 24 - 48 hours using a vacuum siphon and is sent to a reverberatory holding furnace where it is alloyed, fluxed, and degassed to remove trace impurities. There are many different methods used to accomplish this. One method is to add chloride and fluoride salts and then bubble chlorine gas through the molten aluminum. The impurities will react with the chlorine to form hydrogen chloride, aluminum oxide, and metal chlorine emissions.

There are three types of aluminum reduction cells: the prebaked anode cell, and the horizontal and vertical stud Soderberg anode cell (HSS and VSS). All these cells are prepared with petroleum coke mixed with pitch binder to make a paste. The coke is crushed, ground, and screened before being mixed with the pitch binder in a steam jacketed mixer. The paste is added directly to the anode casings of the Soderberg cells, but in the prebaked anode cells it is then baked in a direct-fired ring furnace or an indirectly-heated Reid Hammer furnace. The prebaked anode cells are most common because they are more efficient electrically and they emit fewer organic compounds. There are four pre-baked, two HSS and one VSS facility in Washington.

Methods of Determining Emissions

The most common toxic emissions from potlines are fluorides (especially hydrogen fluoride) and polycyclic organic matter. There is little information available to estimate toxic emissions from aluminum facilities. There are emissions factors available from *AP-42* for gaseous and particulate fluorides for all emission points, as well as for different control scenarios.

A wet scrubber (or a combination of wet scrubbers) is typically used to control gaseous and particulate fluorides as well as particulate matter in all cell types and anode bake furnaces. Additional control devices for particulate matter are wet or dry electrostatic precipitators, multiple cyclones, or dry alumina scrubbers. Gaseous and particulate fluoride can also be controlled by a fluoride adsorption system, which consists of a fluidized alumina bed and filter. The emission stream is passed through the crystalline alumina and then through a filter to catch the entrained alumina dust. The alumina is then recycled back to the potlines. This process has an overall control efficiency of 99%. (*AP-42*). Typical control devices used in Washington facilities are alumina scrubbers, fabric filters, and wet scrubbers.

On October 7, 1997, EPA adopted MACT for primary aluminum production plants. Sources will have between 2 and 4 years to come into compliance with the provisions of the MACT. (New or reconstructed sources are subject to MACT provisions upon startup.) Emissions estimations made after MACT has become effective should be sure to take emissions limitations due to MACT into account. The MACT provisions are found in Part 63, Subpart LL, sections 63.840 - 63.859 of the Code of Federal Regulations.

Secondary Aluminum Production

The process of retrieving aluminum from recycled materials, rather than refining it from bauxite ore, is becoming increasingly popular, especially since the automobile industry has increased its use of aluminum. Producing one ton of aluminum from recycled materials takes 5% of the energy required to refine a ton of aluminum from bauxite ore. (*AP-42*)

Secondary aluminum production consists of two basic processes:

I. Scrap Pretreatment: sorting and cleaning of scraps
II. Smelting/Refining: cleaning, melting, refining, and alloying of aluminum

The process differs for each facility. Plants can have a combination of the processes described here and in a different order, depending on the source of aluminum.

Description of Process

First the scrap is sorted and processed to remove unwanted material such as other metals and plastics. The aluminum metal is then cleaned to remove contaminants by one of these methods: mechanical, pyrometallurgical (heat) or hydrometallurgical (water) cleaning.

The aluminum scraps are then heated and melted in a furnace. Primarily, this is a batch process and is done in a reverberatory furnace. A reverberatory furnace is brick-lined and has a curved roof in which the heat is reflected (reverberated). Other furnaces can be used to hold the melted aluminum and for other processes. The aluminum can go through processes to remove impurities, reduce magnesium content, and combine aluminum with other metals to create an alloy. One process that could potentially produce a lot of toxic emissions is the demagging process. The demagging process involves reducing the magnesium content, and occurs when chlorine and fluorine are injected under pressure into the molten aluminum.

More detailed information on the processes involved in secondary aluminum production can be found in *AP-42*.

Methods of Determining Emissions

There are no emission factors currently available in *AP-42* for toxic emissions from secondary aluminum production.

Emissions from the smelting and refining process can be controlled by fabric filters (baghouses) or electrostatic precipitators. (*AP-42)*

The MACT requirements for secondary aluminum are scheduled to be adopted in 2000.

References

Aluminum Association, Inc., *Aluminum: Know the Facts,* http://www.aluminum.org/ind_indx.htm. Visited November 21, 1997.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 12.1, Primary Aluminum Production, October 1986) (available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Washington State Department of Ecology, *Facility/Site on the Web,* accessed 1/20/98. (http://www.wa.gov/ecology/iss/fsweb/fshome.html)

Other Resources that may be of Interest

Books

World Aluminum Capacity Handbook

Periodicals

Metal Bulletin
Light Age Metal
Mining Journal
Aluminum Statistical Review

Web-Sites

Aluminum Association, Inc. *http://www.aluminum.org/*
American Metal Market (AMM) *http://www.amm.com/index.htm*
EnvironSense (EPA) *http://es.inel.gov/*
Recycling Spent Potliner from Aluminum Smelters *http://es.inel.gov/studies/spent-d.html*
Contact: Bill Ives, Department of Energy's Golden Field Office: (303) 275-4755

Report/Case Studies

Akbar-Khanzadeh, Farhang. *Exposure to particulates and fluorides and respiratory health of workers in aluminum production*, American Industrial Hygiene Association Journal, Akron, Vol. 56, Issue10, **1008**, Oct 1995

Ardal og Sunndal Verk a.s, *Hooded Pots, with Pre-Baked Anodes Allow Gas Collecting Efficiency up to 98%*, EnviroSense Case Study: CS205, Doc. No. 400-013-A-204, Oslo, Norway

Dufresne, A; Loosereewanich, P; Armstrong, B; Theriault, G; Begin, R. *Inorganic particles in the lungs of five aluminum smelter workers with pleuro-pulmonary cancer*, American Industrial Hygiene Association Journal, Akron, Vol. 57, Issue 4, **370**, Apr 1996

Fluorine may pose problems for atmosphere, Chemical Marketing Reporter, New York, Vol. 247 Issue 9, **34**, Feb 27, 1995

Fumeless In-Line Degassing (FILD) of Liquid Aluminum Eliminates Chlorine, EnviroSense Case Study: CS265, Doc. No. 400-103-A-264

Recycling aluminum with 40 percent less energy, Iron Age New Steel, New York, Vol.10 Issue 9, **12**, Sep 1994

Sostrand, Per; Kongerud, Johny; Eduard, Wijnand; Nilsen, Terje; et al. *A test chamber for experimental hydrogen fluoride exposure in humans,* American Industrial Hygiene Association Journal, Akron, Vol. 58, Issue 7, **521**, Jul 1997

Wheeler, David L. "Waste Treatment with a Pay-Back." *Products Finishing*, August 1984: pg. 42

Asphalt Concrete Plants

In Washington, there are approximately 149 facilities that fall under SIC code 2951 Asphalt Paving Mixtures and Blocks (Ecology, 1/20/98).

Description of Process

The asphalt drum mix process involves the grading and storing of various rocks and sands for mixing and conveying to a rotary kiln for heating and additional mixing. As the heated product leaves the kiln, it is combined with refined petroleum to form the finished product. This material is then conveyed to large overhead hopper bins for storage prior to being loaded into delivery trucks.

Method of Determining Emissions

The most common toxic emissions from asphalt concrete plants are from acetaldehyde, acetone, benzene, ethyl benzene, formaldehyde, toluene, and xylene (*AP-42*[1], Section 11.1).

The most common emission control system at these asphalt plants is a baghouse and a wet scrubber. Exhaust gases from the process are manifolded through a wet scrubber to remove the particulates before being vented to the atmosphere from a circular or rectangular exhaust stack.

If plant-specific source tests are not available, *AP-42* contains emission factors for organics and metals, as well as criteria pollutants.

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[1] U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, October 1997, Document No. AP-42.

References

Eureka Laboratories, *Compilation of Air Toxics Pollutant Emission Factors Volume II B: Technical Support Information Asphalt Concrete Plants*, 1991 Edition, January 1991. Prepared for Central Valley Rock, Sand & Gravel Association.

National Asphalt Pavement Association, *Evaluation of Stack Emissions from HAM Facility Operations*, December 1993, Special Report 166. NAPA Building; 5100 Forbes Boulevard; Lanham, Maryland 20706-4413;

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 11.1 Hot Mix Asphalt Plants, January 1995) (available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Washington State Department of Ecology, *Facility/Site on the Web*, accessed 1/20/98. (http://www.wa.gov/ecology/iss/fsweb/fshome.html)

Boilers

There are two types of boilers, internal and external combustion. External combustion occurs when the combustion air is present at or near atmospheric pressure. Internal combustion occurs in turbines (same as jet engines) where the incoming air is compressed before being mixed with the fuel. Boilers can be broken down in three categories: commercial, as in heating buildings; industrial, for manufacturing facilities; and electrical, for generation of electricity.

All boilers consist of 4 main parts: burner, firebox, heat exchanger, and a method of fuel flow. Larger boilers also include auxiliaries, which may include a flame safety device, soot blower, air preheaters, economizer, superheater, fuel heater, or automatic flue gas analyzer. (*AP-40*, 553)

There were a total of 333 boilers reported in 1995 to the Ecology database, Washington Emissions Data System. Due to lack of throughput data, the total energy produced from each of the fuel types could not be determined. However, information on the number of boilers and some reported emissions were available. Figures 1-2 show what percent of fuel types were used in these boilers and what percent fall into each of the categories listed above.

Note that the commercial category does not include all of the commercial boilers in the state because that data is not available. Also, PSAPCA reports boilers in their jurisdiction by segment, one segment for each fuel used. Because of the lack of throughput data, the main fuel for these boilers cannot be determined. Therefore, the number of boilers by fuel does not add up to the number of actual boilers present.

Natural gas powers a large number of the boilers, and also accounts for a large percentage of the power generated by boilers in Washington State. In terms of megawatts produced, lignite is in second place followed closely by wood. (*Air Toxics Emissions Estimation Methods Evaluation*, 1)

The four sub-sections of this chapter describe combustion from four fuel sources:
1. Wood-Waste
2. Oil (Distillate or Residual)
3. Coal (butiminous/subbituminous or lignite)
4. Natural gas

Other fuels used in Washington state include process gas, solid waste, liquified petroleum gas (LPG), and kerosene/naphtha (jet fuel).

Figure 1. Number of Boilers for each Fuel Type

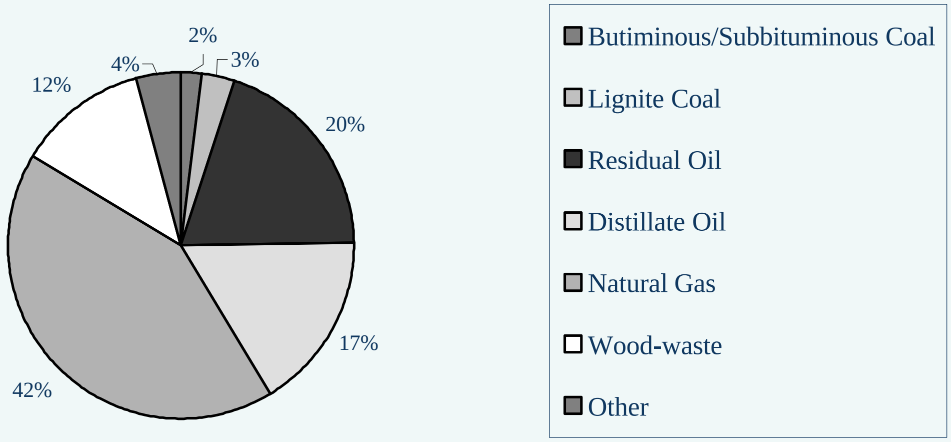


Figure 2(a). Number of External Combustion Boilers in Each Category

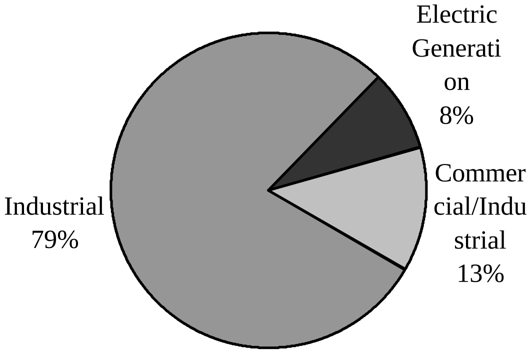
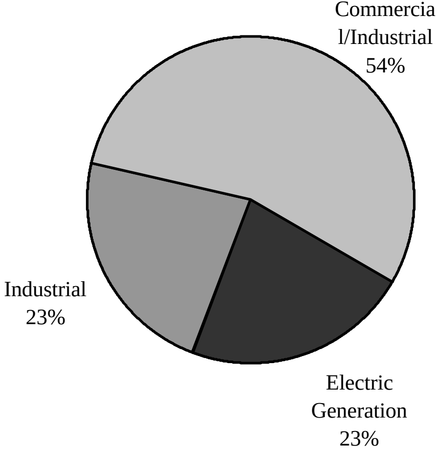


Figure 2(b). Number of Internal Combustion Boilers in Each Category



EPA updated all the boiler sections in *AP-42*[1] in October 1996. Information on boilers which combust specific types of fuel can be found in that report in the following sections:

Section 1.1	Bituminous and Subituminous Coal
Section 1.3	Fuel Oil Combustion
Section 1.4	Natural Gas Combustion
Section 1.6	Wood Waste Combustion in Boilers
Section 1.7	Lignite Combustion

This update includes emission factors for toxics such as polychlorinated, polynuclear aromatics, organics, acid gases, trace metals, and controlled toxics.

The Clean Air Act requires development of regulations for toxic air emissions from several categories of industrial combustion sources, including boilers, process heaters, waste incinerators, combustion turbines, and internal combustion engines. The EPA has started Industrial Combustion Coordinated Rulemaking (ICCR) to develop recommendations for MACT regulations that address the various combustion source categories and pollutants. The ICCR is expected to provide its recommendations to the EPA by the year 2000. Regulations will be developed under sections 111, 112 and 129 of the Clean Air Act.

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[1] U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, October 1997, Document No. AP-42.

References

U.S. Environmental Protection Agency, *Air Pollution Engineering Manual*, Second Edition, May 1973, Document No. AP-40.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Washington State Department of Ecology, *Air Quality Program database*, 1995. Contact: Sally Otterson, 360-407-6806.

Wood Waste Boilers

According to a recent Ecology survey there are currently 85 wood-waste boilers in Washington State. These boilers combust about 3.3 million tons of wood annually, which accounts for 64% of all the fuel combusted in wood-waste boilers. The other fuels burned include refuse-derived fuel, old corrugated cardboard, tire-derived fuel, pulp mill sludges, natural gas, coal, and oil. Of those that combust fuels other than wood (therefore, excluding those that are burn wood-waste only) about one-half of the fuel combusted are other fuels. (DeMay, p. 2-7)

Description of Process

Waste wood in the form of chips, sawdust, shavings, sander dust, hogged wood or bark is fired in a boiler to obtain heat. Depending on the boiler type, the fuel may also include other waste materials that get entrained in the fuel conveyor system such as soil, rocks, rags, and metal parts and pieces. The operator may also burn oil along with the wood waste, especially when the wood is wet, to supplement the heat content of the fuel.

The predominant species of wood burned in the western part of the state are Douglas fir, spruce, western red cedar, cottonwood and hemlock. In eastern Washington the mix of species is markedly different: ponderosa pine, Douglas fir, white fir and a small (1-5%) quantity of western red cedar.

The moisture content of the fuel is typically between 40-50% by weight. Facilities which store the fuel outside have a problem with fuel moisture in the winter, in which moisture content may be up to 60-70%.

Wood that has been transported or stored in salty or brackish water creates salt-laden wood. Combustion of salt-laden wood increases fine particulate loading and plume opacity as well as air toxics such as dioxin. About 24% of the wood waste boilers in Washington combust some salt-laden wood. (DeMay, p. 7)

In Washington, wood-waste boiler types include pile burners (dutch and fuel cell oven), spreader-stokers (mechanical and pneumatic), suspension burners, and fluidized bed. Figure 3 below shows the number of each type in Washington. The most common use of the wood-fired boilers in the state is in industry for the production of steam for process use. Wood-fired boilers are also used for cogeneration (production of steam for both process use and for electric generation).

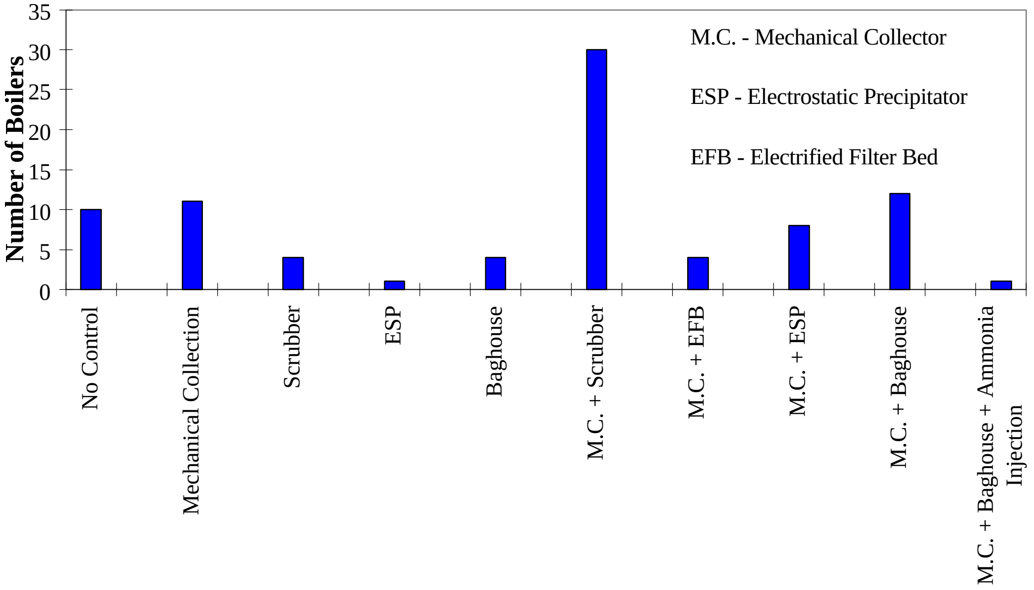
Figure 3. Wood-Waste Boiler Design Distribution in Washington State[2]
(DeMay, Table 7, pg. 18)

Types of Boiler Design	No. of Boilers	%
Spreader Stoker	24	38
Dutch Oven	22	34
Fuel Cell	13	20
Fluidized Bed	2	3
Other	3	5

Method of Determining Emissions

The existing emission control equipment for wood-fired boilers in Washington is exclusively for particulate control. In pulp mills and larger facilities, electrostatic precipitators may be used. Most of the wood waste boiler population is controlled with either cyclones or wet scrubbers, and less commonly with fabric filters (baghouses). Figure 4 shows the control equipment present in Washington State.

Figure 4. Air Pollution Control Equipment[3] (DeMay, Graph 4, pg. 14)



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[2] Note: 64 out of 85 boilers reported.
[3] Note: 64 out of 85 boilers reported.

Typically, flyash reinjection is also practiced in some of the 1970 generation boilers and newer. The main purpose of flyash reinjection is to improve fuel efficiency, though it does increases particulate emissions. Of Washington wood-waste boilers, 32% use flyash reinjection (only 86% of boilers reported).

Only a few of the boilers in the state are equipped with automatic controls. Proper combustion and low air emissions, even in those that are equipped with automatic controls, is largely dependent on the skill and experience of the boiler operator. Conversations with facility personnel indicate that there is currently no recognized training program for boiler operators. Training, for most facilities, occurs on the job.

Fuel storage is also an important parameter. Facilities that have covered storage areas for their fuel may have fewer moisture problems in the winter.

The Washington State Department of Ecology is currently undergoing a Reasonably Available Control Technology (RACT) analysis for the source category of Wood-fired Boilers. The likely outcome of this analysis could include new air emission limitations for both toxic and criteria pollutants.

If no mill-specific source tests are available, toxic emission factors are available from *AP-42* or *NCASI* (1995) for these sources.

References

Atkins, R.S, C.T. Donovan, and J.M Peterson. *Wood Products in the Waste Stream: Characterization and Combustion Emissions Vol.1.*, New York State Energy Research and Development Authority, March 1993.

California Air Resources Board, *Test Report No. C-87-042*.
California Air Resources Board, *Test Report No. C-88-050*.
California Air Resources Board, *Test Report No. C-88-065*.
California Air Resources Board, *Test Report No. C-88-066*.

DeMay, James, *Wood Waste Boiler Survey*, April 1997, Publication No. 97-204. Washington State Department of Ecology.

Hubbard, A.J. *Hazardous Air Emissions Potential from a Wood-Fired Furnace*, Wisconsin Department of Natural Resources.

Emery, John, American Wood Association. Personal communication.

Kleindienst, T.E., P.B. Shepson, E.O. Edney, L.D. Claxton, and L.T. Cupitt. *Wood Smoke: Measurement of Mutagenic Activities of Its Gas- and Particulate-Phase Photooxidation Products*, Environmental Science and Technology, 20, May 1986, 493-501.

National Council of the Paper Industry for Air and Stream Improvement (NCASI), *Technical Bulletin No. 650*.

National Council for the Paper Industry for Air and Stream Improvement (*NCASI*), Inc. *Compilation of 'Air Toxic' and Total Hydrocarbon Emissions Data for Sources at Chemical Wood Pulp Mills*, October 1995. Technical Bulletin No. 701: Volumes 1 and 2.

Nielsen, P.A., *Emission of PAH and Mutagenic Activity from Furnaces Fueled with Cereal Straw or Wood Chips*, Chemosphere, 23, No. 6, 1991, 723-735.

Sassenrath, Charles, *Air Toxic Emissions from Wood Fired Boilers*, TAPPI Environmental Conference, 1991.

Shoemaker, D.P., C.W. Garland, J.I. Steinfeld, and J.W Nibler, *Experiments in Physical Chemistry*, 4th. Ed., Mc-Graw Hill, Inc., 1981.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 1.6, Wood Waste Combustion in Boilers, October 1996) (available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Washington State Department of Ecology, *Facility/Site site on the Web*, accessed 1/20/98. (http://www.wa.gov/ecology/iss/fsweb/fshome.html)

Word, David, National Council of the Paper Industry. Personal conversation.

Appendix
Alternate Methodology[4]

Wood waste boiler emissions are subject to more local variables such as fuel type, mix and moisture content than the other categories. Emphasis was placed on characterizing emissions from wood waste boilers. A database was created which contains 76 wood waste boiler source test runs conducted either in Washington or on the West Coast.

To characterize the population and operation of boilers in Washington, Ecology staff surveyed and visited nine facilities including sawmills, plywood manufacturers, an electric generating facility and a pulp and paper mill. These facilities are located throughout the state and account for thirteen boilers. A literature search was conducted in addition to site visits, and conversations with boiler operators, local air personnel, and other state and federal agency staff. This information is included in the bibliography. Source tests from in and out of state were obtained and are also reflected in the bibliography.

The FIRE database contains the latest EPA emission factors based on section 1.6, supplement F of AP-42, released in April 1993.

One of the greatest misgivings of the current FIRE/AP-42 database is the wide numerical range of calculated emission factors per species. For example, benzene emission factors range from 8.6 E-5 to 1.4 E-2 lb/ton. For a 'typical' 100 MMBTU/hr wood waste boiler in Washington this range translates to 13.9 lbs. versus 1.14 tons per year. This range places the user in a predicament of picking a number "out of the air". Typically, regulatory agencies use the high end of the range to base decisions on. The following proposed estimation methods result in narrowing the range for each emission type.
AP-42 and FIRE utilize a variety of units:

- pounds per ton of fuel burned (lb/ton)
- pounds per million BTU input (lb/MMBTU)
- milligrams per metric ton (mg/tonne)
- milligrams per kilogram (mg/kg)

The energy input emission factor is based on the following assumptions:

* Heating value: 4500 Btu/lb of wood.
* Moisture content: 50%
* F Factors[5] of 9240 dscf/MM Btu for wood and 9600 dscf/MM Btu for bark

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[4] This analysis was presented in the first edition of this report. Since then, new toxic emission factors are not available. However, the analysis is still relevant and is included here in it's original form. Explanatory footnotes have been added where needed.

[5] A F-factor is "a factor representing a ratio of the volume of dry flue gases generated to the caloric value of the fuel combusted." (40 CFR Part 75 Appendix F 3.3.5)

In fact, heating value for the fuel used in our state deviates widely (4000-10000 BTU/lb). The systematic error interval produced from just the heating value is 136% of the calculated value. In other words, for an emission factor of 0.014 lb X[6]/MM Btu, the uncertainty interval is equal to 0.019 lb X/MM Btu. Note that this uncertainty interval was calculated only taking into account the heating value variation.

There are other factors that vary dramatically such as moisture, boiler efficiency, F-factors (due to the heterogenous nature of wood waste), and fuel mix. Probably the greatest error is introduced in the estimation of the mass of wood burned. None of the facilities weigh the wood waste before burning it. Only in one of the facilities visited is the mass of wood bought actually measured because they pay the suppliers based on the weight delivered to the storage area where it is piled up. However, even that facility does not weigh the wood waste before burning it.

Due to degree of error propagation described above, units of pounds per million BTU output are recommended for a facility-specific emission factor. The pounds of steam produced is an operating boiler datum readily available; therefore, factors with units of lb/MMBTU can more accurately reflect emissions.

Gaseous Emissions

The many compounds in the gas phase emitted from boilers have not been consistently characterized. Much attention has been focused on benzene and formaldehyde since both are known carcinogens. Although the bulk of the gaseous emissions exhibit low toxicity, Kleindienst et.al. have demonstrated that the mutagenic activities of the gas-phase (and the particulate phase) species such as propylene and toluene increase significantly upon irradiation in the presence of nitrogen oxides (NOx). Note that these compounds are ubiquitous in an urban environment mainly due to mobile source contributions. Since hydrocarbons are products of incomplete combustion, theoretically, carbon monoxide could be used as a surrogate.

Indeed, three studies (Hubbard, Sassenrath, and Atkins, et.al.) have found a linear, but not absolute correlation. The variability in gaseous emissions can not be explained solely by carbon monoxide variability. The preponderance of the data does follow theory especially for benzene and formaldehyde. For other compounds such as acetaldehyde, benzaldehyde, salicylaldehyde, acrolein, and certain individual polycyclic aromatic hydrocarbons (PAHs) the correlation does not hold. In most cases this is probably due to very small data sets, high blank values, and below detection limit calculations based on half of the detection limit.

Since the available data on other compounds of gaseous organic emission data is so sketchy, it is not possible to develop emission factors for any of them for the category as a whole. AP-42/FIRE do contain emission factors for more gaseous emissions compounds; however, as explained above their use is not recommended, especially in the case of factors developed from data sets smaller than four runs.

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[6] X is used to refer to any toxic, and is just used as an example.

The tables presented below were developed based on data collected in Atkins, et. al. which contains a comprehensive summary of the wood-fired boiler data collected to date. The 95 percentile confidence intervals were calculated from the standard deviation of the sample data. Propagation of random error was accomplished through propagation of variance equations (Shoemaker,et.al.).

Table 1. Recommended Benzene Emission Factors for Wood/Bark Fired Boilers and Associated 95% Confidence Interval

Units Benzene	CO Range corrected to 12% CO_2 0-200 ppm	CO Range corrected to 12% CO_2 200-500 ppm	CO Range corrected to 12% CO_2 500-1500 ppm
lbs/MMBTU (in)	6.9 E-5 +/- 3.5 E-5	6.9 E-4 +/- 4.0 E-4	2.0 E-3 +/- 1.1 E-3
lbs/MMBTU(out)[a]	1.2 E-4 +/- 1.0 E-4	1.2 E-3 +/- 1.0 E-3	3.4 E-3 +/- 2.9 E-3

[a] Based on a boiler efficiency of 60%, the 95% confidence interval includes propagation of error for boiler efficiency ranging from 40-80%

Table 2. Recommended Formaldehyde Emission Factors for Wood/Bark Fired Boilers and Associated 95% Confidence Interval

Units Formaldehyde	CO Range corrected to 12% CO_2 0-200 ppm	CO Range corrected to 12% CO_2 200-500 ppm	CO Range corrected to 12% CO_2 500-1500 ppm
lbs/MMBTU (in)	6.3 E-4 +/- 3.5 E-5	1.0 E-3 +/- 4.0 E-4	2.1 E-3 +/- 1.1 E-3
lbs/MMBTU(out)[a]	1.1 E-3 +/- 8.6 E-4	1.7 E-3 +/- 1.3 E-3	3.4 E-3 +/- 3.2 E-3

[a] Based on a boiler efficiency of 60%, the 95% confidence interval includes propagation of error for boiler efficiency ranging from 40-80%

Particulates and Semi-volatiles
More emission source tests are available from well controlled rather than uncontrolled sources. Most of the source tests conducted to date on wood waste boilers are to determine total particulate emissions.

Trace metals are part of wood tissues. During combustion the metals become partitioned between the bottom ash and the fly ash. The metals fly ash emissions from wood combustion are generally insignificant. For example, emission factors for cadmium, chromium, manganese and nickel range from 1 E-7 to 1 E-5 lb/MMBTU for multiclone-controlled boilers with no flyash reinjection. For a 'typical' 100 MMBTU/hr wood waste boiler in Washington this range translates to 0.53 lbs. versus 48 lbs. per year.

Flue gas emissions of most trace metals (except for mercury) have been correlated to the particulate emissions (Atkins, et.al.). Metal emissions in the stack gas are directly related to the efficiency of the particulate control device. Electrostatic precipitators achieve the highest removal efficiency, followed by wet scrubbers and multiclones. The FIRE/AP-42 emission factors do not account for this correlation diminishing their utility. A comprehensive summary of the metals flue gas emissions data is available (Atkins, et.al.). Table 3 emission factors were calculated using that data. Uncertainty intervals were not calculated.

Table 3. Recommended Metal Emission Factors

Element	TSP 0-0.005 gr/dscf corrected to 12 % CO_2	TSP 0.005-0.01 gr/dscf corrected to 12 % CO_2	TSP 0.01-0.005 gr/dscf corrected to 12 % CO_2
Arsenic	1.8 E-7	7.1 E-7	1.1 E-5
Beryllium	1.7 E-7	1.9 E-7	2.1 E-7
Cadmium	4.4 E-7	3.5 E-7	1.3 E-7
Chromium	1.3 E-6	9.4 E-6	8.0 E-6
Hexavalent Chromium	2.6 E-5	N/A	4.0 E-6
Copper	3.0 E-6	N/A	2.4 E-5
Lead	3.2 E-6	2.2 E-5	3.7 E-5
Manganese	4.2 E-5	9.9 E-5	1.3 E-4
Mercury	2.7 E-7	2.6 E-7	7.0 E-7
Nickel	3.0 E-6	3.8 E-6	1.1 E-5
Selenium	2.0 E-6	N/A	2.5 E-6
Zinc	6.0 E-5	N/A	3.8 E-4

The semi-volatile emission species studied include PAHs, dioxins and furans. The review of emission factors for these species has not been completed, and is pending analysis of the Ecology database.

Proposed Estimation Method

Two approaches are proposed. The most accurate approach is for each individual facility to source test each unit for the individual compounds of interest. The operating parameters that must be recorded at the time of testing are: pounds of steam generated per hour, pressure and temperature of the steam, inlet make-up water temperature and pressure. This data will be used to calculate the energy generated in the boiler with the aid of steam tables. The ratio of underfire and overfire air must also be recorded as well as the percent excess air, percent CO2, CO and O2. In addition, fuel moisture and type are necessary pieces of information. An ultimate analysis of the fuel would be useful. Another hint is to record the name of the boiler operator. If questions arise later about operating parameters, it is useful to have the operator's name.

An example calculation is shown below:

Source test information: 1 lb. of X/hour
Boiler information: 100,000 lbs./hour of steam produced at 200 psia and 400 F
Boiler Operator: Ms. Jane Smith

Temperature of water coming in: 70 F at atmospheric pressure

From steam tables: Enthalpy of steam (out)= 1240.6 Btu/lb
Enthalpy of water (in) = 38.05 Btu/lb

Total energy out in Btu = 100,000 lbs./hr (1240.6-38.05 Btu/lb.) = 1.2 E8 Btu = 120 MMBTU (out)/hr

Facility-specific emission factor: 1 lb. of X/ 120 MMBTU = 8.3 E-3/MMBTU (out) when burning fuel of Y moisture and Z type, at R ratio of underfire and overfire air, A% CO2, B% excess air, C% O2, and D% CO.

The second approach is to use tables 1-3 to estimate benzene, formaldehyde, and metals emissions. Note that to use these tables it is necessary to know the carbon monoxide and particulates concentration typically emitted from the facility. An average of the source tests performed recently is appropriate. A CO continuous emission monitor is advisable. If the boiler efficiency is known, divide the emission factor based on inlet Btu's (lbs/MMBTU (in)) by the efficiency, and then multiply the total Btu's produced from the boiler to obtain the estimated pounds of pollutant X emitted. If boiler efficiency is not known, use the factor based on total BTU output.

Speciation of gaseous emissions requires the use of a variety of different analytical techniques. The measurement methodology is still evolving for some compounds.

Contribution of HAP Emissions from Wood-Fired Boilers in Washington

Statewide benzene and formaldehyde emissions were estimated. The estimate was based on 43% of the boilers operating at CO levels between 0-200 ppm, 26% between 200-500 ppm, and 31% greater than 1500. These percentages were calculated from the Ecology database[7]. In reality, it is expected that the percentage operating between 200-500 ppm CO is higher because the database contains some runs which purposely intended to reflect poor combustion conditions (such as when grate cleaning or soot blowing). The estimated pounds per year from all the wood-fired boilers in Washington of benzene and formaldehyde were 1950 and 2710, respectively.

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[7] Refers to Ecology's Washington Emissions Data System (WEDS).

Distillate and Residual Oil Boilers or Oil Backup

Description of Process

There are two main types of oil used in boilers in Washington state: residual oil and distillate oil. Distillate oil (includes kerosene and diesel) is more volatile than residual and is usually used in domestic or small commercial boilers. Residual oil is more viscous than distillate and is usually used in electric generation, industrial and large commercial boilers.

Combustion of the various oil grades (light distillate to residual) requires different burner technology due to the large specific gravity range (from below zero to more than 90 degrees API). Heats of combustion also vary widely (17,000-20,500 Btu/lb). Sulfur, inert and impurity content depends on the place of origin of the oil. The main boiler configurations include water tube, fire tube, cast iron, and tubeless.

Method of Determining Emissions

The boiler configuration and size, fuel type and composition, and combustion practices affect emissions. Organic toxic emissions are mostly dependent on combustion efficiency.

If no mill-specific source tests are available, toxic emission factors are available from *AP-42* for these sources.

References

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 1.3, Fuel Oil Combustion, October 1996)
(available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Washington State Department of Ecology, *Facility/Site site on the Web*, accessed 1/20/98.
(http://www.wa.gov/ecology/iss/fsweb/fshome.html)

Coal-Fired Boilers

Description of Process

There are many different ranks of coal including the most common: lignite, anthracite, bituminous, and subbituminous. The coal's volatile matter, fixed carbon, inherent moisture, and oxygen determine the rank. Generally, increasing in rank increases the fixed carbon and decreases the volatile matter and moisture.

In Washington state, coal-fired boilers use three types of coal: bituminous, subbituminous and lignite. Figure 5 shows the heating values for these coal-types.

Figure 5. Heating Values In British Thermal Units (Btu) /Pound
(*AP-42*, Sections 1.1 and 1.7)

Basis	**Lignite**	**Bituminous**	**Subbituminous**
Wet, mineral-matter free		10,500-14,000	8,300-11,500
Wet	5,000-7,500		
As-mined		10,720-14,730	9,420-10,130

Boilers can be classified by their heat transfer method type and arrangement and their firing configuration. Heat transfer methods include water tube (most common), fire tube, and cast iron, which can be arranged in horizontal, vertical, straight or bent tube position. The firing configuration can be either suspension, stoker, or fluidized bed.

The Pacific Power and Light Company, Centralia Steam Electric Generating Plant is the largest source in this category in the state.

Method of Determining Emissions

Emissions are affected by rank and composition of coal, type and size of boiler, combustion conditions, load, and equipment maintenance.

Organic toxic air emissions depend on what chemicals are present in the coal and are products of incomplete combustion (PIC). Organic toxics can take the form of dioxins and furans, and polycyclic organic matter (POM).

Metals, such as manganese, beryllium, cobalt, chromium, arsenic, cadmium, lead, antimony, mercury, and selenium, are also products of coal combustion and are controlled by particulate controls such as electrostatic precipitators (ESP), fabric filters, wet scrubbers, cyclones, and side stream separators.

Other common toxic emissions from coal combustion are hydrogen fluoride, fluorine, hydrogen chloride, and chlorine. The hydrogen chloride and fluoride can be controlled using an acid gas scrubbing system.

AP-42 classifies trace metal emissions into the following three classes (*AP-42*, 1.1-5):

> "Class 1: Elements that are approximately equally concentrated in the fly ash and bottom ash, or show little or no small particle enrichment. Examples include manganese, beryllium, cobalt, and chromium.
> Class 2: Elements that are enriched in fly ash relative to bottom ash, or show increasing enrichment with decreasing particle size. Examples include arsenic, cadmium, lead and antimony.
> Class 3: Elements which are emitted in the gas phase (primarily mercury, and in some cases, selenium).

Control of Class 1 metals is directly related to control of total particulate matter emissions, while control of Class 2 metals depends on the collection of fine particulate. Because of variability in particulate control device efficiencies, emission rates of these metals can vary substantially. Because of the volatility of Class 3 metals, particulate controls have only a limited impact on emissions of these metals." (*AP-42*)

Other controls techniques that can be used to reduce criteria emissions are fuel treatment or substitution (generally controls SO_2), combustion modification (generally NOx and some PM), and post combustion control.

If no mill-specific source tests are available, emission factors are available from *AP-42* for dioxins and furans, speciated PAHs, aldehydes and other organic compounds, hydrogen chloride, hydrogen fluoride, and metals.

Reference

Mrazek, S. Southwest Air Pollution Control Agency, facsimile 3/15/94.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources,* Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 1.1, Bituminous and Subituminous Coal, Section 1.7, Lignite Combustion, October 1996)
(available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Washington State Department of Ecology, *Facility/Site on the Web,* accessed 1/20/98.
(http://www.wa.gov/ecology/iss/fsweb/fshome.html)

Natural Gas Boilers and Turbines

Description of Process

Natural gas is the main fuel used to generate power in the state. Gas turbines are used extensively in Washington for natural gas pipeline compression and power generation.

If no mill-specific source tests are available, toxic emission factors are available from *AP-42* for these sources.

References

Pavri, R.E. and R.A Symonds. "Unburned Hydrocarbon, Volatile Organic Compound, and Aldehyde Emissions from General Electric Heavy-Duty Gas Turbines." presented at the *Gas Turbine and Aeroengine Congress and Exposition Held in Brussels, Belgium June 11-14, 1990*.

Todd, D. "Emissions Tests on Natural Gas-Fired Utility Boilers at Three Power Plants." California Air Resources Board, December 1991.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources,* Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 1.4, Natural Gas Combustion, October 1996)
(available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Washington State Department of Ecology, *Facility/Site on the Web,* accessed 1/20/98.
(http://www.wa.gov/ecology/iss/fsweb/fshome.html)

Chemical Pulp Mills

Pulping is the term used for the process which separates wood fibers. Chemical pulping, dissolving the lignin in the wood to create a pulp, is the most commonly used pulping process. Chemical pulping creates higher sheet strength than mechanical pulping; however, yields 40 to 50 percent pulp, where mechanical pulping yields 95 percent pulp.

The two main types of chemical pulping are the more common sulfate pulping (most commonly known as Kraft pulping) and sulfite pulping. Kraft pulping accommodates a variety of tree species, recovers and reuses all pulping chemicals, and creates a paper with a higher sheet strength. Sulfite pulp, however, is easier to bleach, yields more bleached pulp, and is easier to refine for papermaking. The major difference between the two types of chemical pulping is the types of chemicals used to dissolve the lignin. This report will focus mainly on these two types of chemical pulping and bleach plants.

Pulp mills are one of the largest emission sources in Washington and a large toxic pollutant emission producer. There are eight pulp mills in Washington: six Kraft (sulfate) mills and two sulfite mills (one sulfite mill has recently closed).

EPA formally adopted MACT in April 1998 for certain pulping processes. Sources will have between 3 and 8 years to come into compliance with the provisions of the MACT. Emissions estimations made after MACT has become effective should be sure to take emissions limitations due to MACT into account. The MACT provisions are found in Part 63, Subpart S, sections 63.440 - 63.459 of the Code of Federal Regulations. MACT requirements for combustion sources at pulp and paper mills will be subject to a separate MACT.

Kraft (Sulfate) Pulping

The Kraft process was developed in Germany in 1879 and was first applied to a Swedish mill in 1885. The resulting paper was much stronger than any paper previously made, and therefore the process was named “Kraft”, (German and Swedish for “strength”). (MacDonald, 349) Kraft pulping creates dark brown paper which is used for boxes, paper bags, and wrapping paper. Kraft pulp can also be used for writing paper and paperboard when bleached, and for diapers when fluffed.

The three main steps involved in Kraft pulping are:
1. Digestion: wood chips are cooked
2. Washing: black liquor is separated from the pulp
3. Chemical recovery: chemicals are recovered from the black liquor for reuse

Turpentine and tall oil may also be recovered for use or resale. This process is covered briefly in the Digestion section.

Description of Process

1. Digestion

The first step in pulping wood is to "cook" the wood chips. A digester, heated by steam, "cooks" the wood chips in *white liquor* (a mix of sodium hydroxide (NaOH) and sodium sulfide (Na_2S)) until done. The cooking process dissolves most of the *lignin*[1] and only some of the *hemicellulose*[2], leaving mostly *cellulose*[3] to hold the fibers together. The digester system may be a batch or a continuous process.

Relief gases are vented continuously from the digester, which helps remove air and other non-condensable gases and reduce the pressure at blow, when the pulp is discharged to the blow tank. After the cooking process, the pulp and *black liquor* (the chemical mix left after the cooking process) are discharged to a blow tank.

By-products can be recovered from the digestion process. For example, turpentine distills with water out of the blow tank and the evaporators and is separated to be used. The resin acids and fatty acids dissolved from the wood form sodium soaps which are skimmed off the black liquor from storage tanks, evaporators, and black liquor oxidation tanks, and then acidified with sulfuric acid to form tall oil.

Before the washing process, the pulp is usually sent to deknotters, screens used to remove knots (large pieces of fiber not completely broken down in the digester).

2. Brownstock Washing

Pulp from the blow tank and deknotter is washed with water in a process commonly called *brownstock washing*. Washing removes weak black liquor from the pulp which is sent to the chemical recovery process. This also prevents contamination during subsequent processing steps. Types of washers used include rotary vacuum washer (most common type of washer), diffusion washers, rotary pressure washers, horizontal belt washers, wash press, and dilution/extraction.

All the washer types use water (fresh or recycled) and are usually placed in series to achieve higher removal efficiency.

The rinsed pulp is screened for oversize particles and then excess water is removed. This is done in a gravity thickener (more commonly known as a *decker*).

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[1] "*Lignin* are essentially substituted phenylpropane three-dimensional polymers with the phenylpropane units held together by ether and carbon-carbon bonds." (MacDonald, 36) Lignin makes up 20-35 percent of the wood substance and holds the wood fibers together, giving the wood rigidity.

[2] *Cellulose* and *hemicellulose* are polysaccharides, which make up 60-80 percent of the wood substance. Polysaccharides are high molecular weight carbohydrates. Cellulose is the major component of polysaccharides and is alkali resistant, therefore it is resistant to Kraft chemicals. Hemicellulose is the other portion of polysaccharides and can be dissolved by alkali.

[3] See footnote 2.

3. Chemical Recovery

The reason Kraft pulping is economically successful is that the used cooking liquor can be recovered and reused in the chemical recovery process.

The first step in recovering the chemicals from the black liquor is evaporation. This removes excess water from the black liquor and maximizes the fuel value for the recovery furnace.

There are two types of evaporators generally used in the chemical recovery process: direct (DCE) and indirect (NDCE) contact evaporators. Some types of DCE include the multiple-effect evaporator (most common), flash evaporation and thermocompressor evaporation. DCE use heat from direct contact with the recovery furnace flue gases, while NDCE uses indirect contact.

Black liquor oxidation is needed after DCE, but not after NDCE. After DCE, the black liquor is normally oxidized with air to control the sulfide level and prevent the release of odorous compounds. This is done by countercurrently passing the black liquor through an air stream using a porous diffuser, sieve tray tower, packed tower or agitated air sparge. The oxidation reaction converts sodium sulfide (Na_2S) to sodium thiosulfate ($Na_2S_2O_3$).

$$2Na_2S + 2O_2 \rightarrow Na_2S_2O_3 + 2NaOH$$

After NDCE or black liquor oxidation, the black liquor is then forced through spray nozzles into the recovery furnace, where it is burned providing heat to generate steam. This also conserves the inorganic chemicals, which create a molten smelt on the floor of the furnace.

The molten smelt, composed of sodium sulfide and sodium carbonate, is drained from the recovery furnace hearth through smelt spouts. In a smelt dissolving tank, the smelt is quenched with water, producing *green liquor*.

Sodium carbonate from the smelt is then converted to sodium hydroxide in the causticizer by adding calcium hydroxide. The calcium carbonate resulting from the reaction precipitates from the solution and is collected and sent to the lime kiln where it is converted to lime (calcium oxide). The calcium oxide is then slaked to produce calcium hydroxide for reuse in the causticizer.

Methods of Determining Emissions

1. Digestion

Relief gases from the digestion process are usually treated by incineration. The emissions are affected by temperature, moisture content, flow rate and variability, sulfur gas and organic material concentrations, and flammability limits.

Gases from the blow tank are typically controlled using either a direct contact or surface condenser. Emissions are mainly affected by the frequency of blow. Batch digesters have higher emissions since the gases are released in surges rather than continuously, making the gas volume larger and harder to control. Major toxic emissions from blow tanks are methanol, acetone, and methyl mercaptan (*AP-42*[4]).

Tall oil recovery vents for continuous and batch systems are typically controlled by a white liquor scrubber.

Deknotter emissions are affected by residence time and the exposure of pulp to air. The major toxic emission from the deknotters is methanol. (*AP-42)*.

Mill-specific source tests should be used where available, as there are no toxic emissions information available from *NCASI* and only hydrogen sulfide emission factors from *AP-42* for this source. *AP-42* provides information on particulate, sulfur dioxide, and carbon monoxide emissions.

2. Brownstock Washing

In the washing process, toxic emissions volatilize from the pulp and black liquor. Brownstock washers are typically controlled by incineration because the gas stream is small and incineration is most practical. Emissions mainly depend on the pulp production and type of digestion (batch or continuous). Different washer types will also affect the emissions depending on their contact with air, as enclosures vary. The largest toxic emissions from brownstock washers are from methanol, acetone, and acetaldehyde (*NCASI*).

Emissions from the decker hood vents and screens may be affected by residence time, air exposure, and equipment design and age. Fugitive toxic emissions from these sources include acetone, dimethyl disulfide, methyl mercaptan, methanol, ethanol, o-cresol and dimethyl sulfide (*AP-42* and *NCASI)*.

Mill-specific source tests should be used where available. Toxic emission factors are available from *NCASI*[i] for these sources.

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[4] U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, October 1997, Document No. AP-42.

Chemical Recovery

DCE have higher emissions than NDCE due to direct contact of flue gases with liquor. Controls include condensation, liquid scrubbing, and thermal oxidation. Factors affecting the emissions are black liquor quality, chemicals used, evaporator design, temperature, moisture content, flow rate and variability, and flammability limits. Toxic emissions from an evaporator include methanol, acetone, dimethyl disulfide, dimethyl sulfide, and methyl mercaptan (*AP-42*).

Gaseous emissions from black liquor oxidation are controlled by incineration. Emissions are affected by liquor type (weak or strong), and oxidation contacting method and efficiency. Toxic emissions include methanol and acetone (*AP-42*).

Recovery furnaces are typically controlled by either wet bottom or dry bottom electrostatic precipitators, sometimes followed by a wet scrubber. Emissions are affected by precipitator design and combustion conditions. Trace metal emissions are dependent on the type of wood pulped and also the intensity of combustion (indirectly the temperature) and particulate collection efficiency. Toxics emissions from a recovery furnace include methanol, hydrochloric acid, dioxins and furans, metals, chloromethane, trichlorofluoromethane, acetaldehyde, and acetone (*AP-42* and *NCASI*).

Particulate control devices on smelt tanks are usually mist eliminators (demisters) that may be used in combination with a spray or packed tower scrubber. Alternate control devices include venturi scrubbers, cyclone spray scrubbers, or packed tower scrubbers. Smelt tank organic compound emissions are affected by the quality of the water used for dissolving the smelt, the quality of the vent gas scrubbing medium, and the residence time in the tank. Toxic emissions include methanol, formaldehyde, valeraldehyde, acetaldehyde, ammonia, dimethyl disulfide, dimethyl sulfide, and methyl mercaptan (*AP-42*). The largest toxics emissions from a smelt tank are methanol, formaldehyde, valeradehyde, acetaldehyde, and methyl mercaptan (*NCASI*).

Lime kilns are most commonly controlled by wet scrubbers (venturi scrubbers) but can also be controlled by mist eliminators and/or electrostatic precipitators. Lime kiln emissions may be affected by concentration of organic constituents in the scrubbing medium is perhaps the most important factor. The level of organics in water or condensate used for lime mud washing, the fossil fuel combusted, and the efficiency of combustion also contribute to emission levels. The toxic emissions include naphthalene, methanol, formaldehyde, acetone, dimethyl disulfide, dimethyl sulfide, and methyl mercaptan (*NCASI*).

Mill-specific source tests should be used where available. Toxic emission factors are available from *NCASI*[ii] for these sources.

Sulfite Pulping

The concept of sulfite pulping was created in the United States in 1867, however it was not used in a mill until 1874 by a Swedish chemist who was probably unaware of the U.S. Patent (MacDonald, 277). Sulfite pulping produces a lighter pulp than Kraft pulping. It can be used for newsprint, and when bleached can be used for writing papers and for the manufacture of viscose rayon, acetate filaments and films, and cellophane.

Description of Process

Sulfite pulping follows many of the same steps as Kraft pulping. The major difference in sulfite pulping is that the digester "cooks" with a mixture of H_2SO_3 (sulfurous acid) and HSO_3^- (bisulfite ion in the form of calcium, magnesium, sodium, or ammonium bisulfate). The pulp continues on through the same processes as in the Kraft pulping process.

However, the chemicals separated from the pulp in the washers may or may not go into a recovery process. Chemical recovery in sulfite pulping is practiced only if it is economical. If chemical recovery does occur the liquor goes through an evaporator and then to a recovery furnace. Here, smelt is not formed, but ash and SO_2 are formed.

Method of Determining Emissions

Sulfite mill emissions depend on the base used in the digestion (CaO, MgO, NH_4OH, NaOH), the pH level, and the design of the digester. For calcium-based mills, particulate emissions are controlled by cyclone dust separation system and gaseous emissions are controlled by scrubbing with CaO or $CaCO_3$ slurry. Magnesium-based mills are controlled by a chemical recovery system. Cyclones and scrubbers separate out MgO dust, then the MgO is hydrolyzed to a slurry which is used to scrub SO_2 from the flue gas. For ammonium SO_2 is scrubbed from the flue gas with fresh ammonia solution. Sodium-based mill particulate emissions are controlled by electrostatic precipitators. The largest emissions from a sulfite recovery furnace are methanol, ethanol, vinyl acetate, acetone, and acetaldehyde (*NCASI*).

Mill-specific source tests should be used where available. Toxic emission factors are available from *NCASI*[iii] for these sources.

Bleaching

Description of Process

The purpose of the bleaching process is to enhance the physical and optical qualities (whiteness and brightness) of the pulp by removing or decolorizing the lignin. Two approaches are used in the chemical bleaching of pulps. One approach called brightening, uses selective chemicals, such as hydrogen peroxide, that destroy chromatographic groups but do not attack the lignin. Brightening produces a product with a temporary brightness (such as newspaper) that discolors from exposure to sunlight or oxygen. The other approach (true bleaching) seeks to almost totally remove residual lignin by adding oxidizing chemicals to the pulp in varying combinations of sequences, depending on the end use of the product. This creates a longer lasting (sometimes permanent) whiteness, but it weakens the fibers and reduces sheet strength. The most common bleaching and brightening agents are chlorine, chlorine dioxide, hydrogen peroxide and sodium hydroxide.

Typically, the pulp is treated with each chemical in a separate stage. Each stage includes a tower, where the bleaching occurs; a washer, which removes bleaching chemicals and dissolved lignins from the pulp prior to entering the next stage; and a seal tank, which collects the washer effluent to be used as wash water in other stages or to be sewered. Bleaching processes use various combinations of chemical stages called bleaching sequences.

The first stage in the bleaching process is the chlorination stage, whose primary function is to further delignify the pulp. Chlorine reacts with lignin to form compounds that are water-soluble or soluble in an alkaline medium, which aids in delignifying the pulp before it proceeds to the next bleaching stage.

The next stage after chlorination is typically the extraction stage. This stage and the remaining stages serve to bleach and whiten the delignified pulp. The extraction stage removes the chlorinated and oxidized lignin by solubilization in a caustic solution.

Chlorine dioxide is often used in bleaching, either in the chlorination stage (as a substitute for some of the chlorine usage - chlorine dioxide substitution) or as an additional chlorine dioxide stage. Chlorine dioxide has 2.63 times greater oxidizing power (on a pound per pound basis) than chlorine and is used for nearly all high brightness pulps.

The next stage is the actual bleaching stage. Hypochlorite is a true bleaching agent that destroys certain chromophobic groups of lignin. It also attacks the pulp so high cellulose degradation occurs in Kraft pulp. Application of hypochlorite to Kraft pulp is usually used only as an intermediate stage of the sequence or to produce semi-bleached pulps. In the bleach process, residual chlorine must be removed through washing in vacuum washers.

Methods of Determining Emissions

During bleaching, side reactions produce chloroform, phenol, chlorinated phenolics and other chlorinated organics. The bleaching stage has been identified as one of the most significant points of chloroform emissions. Studies conducted by NCASI show that bleaching sequences without hypochlorite have lower chloroform emissions. Chlorine emissions are controlled by scrubbing gaseous emissions with NaOH solution. ClO_2 emissions are controlled by scrubbing gases with alkaline hydrogen peroxide (H_2O_2).

The foremost factor affecting emissions of organic compounds from bleach plants are the level and type of bleaching. Other factors are type of wood bleached, scrubber solutions, scrubber design, bleaching temperatures, and residence time. The toxic emissions from a bleach plant include carbon tetrachloride, chlorine, chloroform, benzene, methanol, methyl chloroform, chlorophenols, phenol, 2,3,7,8-TCDD, and 2,3,7,8-TCDF (*AP-42*).

There is also a new technology to reduce the amount of bleaching chemicals needed, therefore, reducing the amount of emissions. The technology is currently being developed by the Technological Institute in Iceland, Reykjavik, and involves using the enzymes produced by thermophilic organisms to dissolve the lignin in the pulp. The more lignin that can be removed, the fewer chemicals that will be needed in bleaching. (*Chemical Engineering Progress*)

Mill-specific source tests should be used where available. Toxic emission factors are available from *NCASI*[iv] for these sources.

References

Enzymes Tackle Tough Processing, Chemical Engineering Progress, Vol. 92, No. 11, November 1997, pg. 13.

MacDonald, Ronald G. *Pulp and Paper Manufacture. Volume 1: The Pulping of Wood*. 2nd ed., McGraw-Hill, 1969.

National Council for the Paper Industry for Air and Stream Improvement (*NCASI*), Inc. *Compilation of 'Air Toxic' and Total Hydrocarbon Emissions Data for Sources at Chemical Wood Pulp Mills,* October 1995. Technical Bulletin No. 701: Volumes 1 and 2.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources,* Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 10.2, Chemical Wood Pulping, September 1990)
(available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

U.S. Environmental Protection Agency. *Environmental Pollution Control: Pulp and Paper Industry: Part I AIR,* October 1976. EPA 625/7-76-001. Includes an extensive exploration of pulp mill controls and their design.

U.S. Environmental Protection Agency. *General Information Document for the Pulp and Paper Industry*. DRAFT. Washington, D.C.: Office of Air Quality Planning and Standards, July 1991.(No documentation that a final document was ever printed.)

U.S. Environmental Protection Agency. *Pulp, Paper, and Paperboard Industry-Background Information for Proposed Air Emission Standards; Manufacturing Processes at Kraft, Sulfite, Soda and Semi-Chemical Mills,* October 1993. EPA-453/r-93-050a.

Washington State Department of Ecology, *Facility/Site on the Web,* accessed 1/20/98.
(http://www.wa.gov/ecology/iss/fsweb/fshome.html)

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[i] NCASI Technical Bulletin No. 701 is an update of NCASI Technical Bulletin No. 650 (1993), and compiles air toxic data from many different source tests and studies. The new document contains emissions factors for oxygen delignification systems, brownstock washers, deckers, thermal oxidizers, pulp and liquor storage tanks, kraft and sulfite recovery furnaces, lime kilns, smelt dissolving tanks, black liquor oxidation tanks, tall oil reactors, causticizing area vents, bleach plants, paper machines, and wood residue-fired boilers. Discussions of wood residue-fired boilers can be found in the Boiler chapter of this report. The NCASI document lists emissions for each source tested and also gives a median to represent the average emissions as long as at least 50% of the data was above the detection limit. If fewer than 50% of the data were above the detection limit, either the NOR-PLOT median or the SDln median were used. For some processes or air toxics the number of sources tested is limited, therefore caution should be taken when using these data. Ecology does not endorse either of these methods and recommends that the user read the specific cautions listed in the report (NCASI, 26) as the ultimate use of the data will decide what numbers to use. NCASI recommends selecting a source from the list of sources and their

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operating parameters for each unit that most closely represents the emission source you are working with and use that source's emission factors.

[ii] Same as endnote 1.
[iii] Same as endnote 1.
[iv] Same as endnote 1.

Cooling Towers

Industrial process cooling towers recirculate water to cool hot process fluids. The largest cooling towers in Washington are located at petroleum refineries.

Description of Process

Cooling towers are heat exchangers that are used to dissipate large heat loads to the atmosphere. They are used in a variety of settings, including process cooling, power generation cycles, and air conditioning cycles. All cooling towers that are used to remove heat from an industrial process or chemical reaction are referred to as industrial process cooling towers (IPCT). Cooling towers used for heating, ventilation, and air conditioning (HVAC), are referred to as comfort cooling towers (CCT).   Cooling towers are classified as either wet towers or dry towers. Dry towers use a radiator like cooling unit instead of water evaporation. Dry cooling towers, HVAC, and CCT are not included in this report.

Most plants use *indirect contact* cooling. Hot process fluids pass through one or more heat exchangers, condensers, etc., which allow heat to be transferred from the process fluids to the cooling tower water without any contact with the process materials.

Some industries use *direct contact* cooling. Cooling is achieved by placing the water in direct contact with hot materials, picking up surface contaminants like oils and dirt. The warmed water is then is collected, cleaned, (e.g. sent through an oil water separator,) then returned to the cooling tower.

Cooling towers cool the warm water by contacting it with ambient air. The warm water is pumped to the top of the IPCT and is distributed across the distribution deck where it flows through a series of nozzles onto the top of the tower's fill material. Fill material is used in cooling towers to create as much water surface as possible to enhance evaporation and heat transfer. As the water flows down the fill material, it contacts air that is drawn or forced across the fill material by one or more fans at the top of the tower. A small percentage of the water evaporates, cooling the circulating water and heating the air. A smaller portion of the water is entrained in the air stream as droplets of water which are called "drift" if they leave the tower. The warm, moist air then passes through the drift eliminator and exits the tower through the fan stack(s), carrying some residual drift out of the tower. The cooled water falls into a cold water basin, which typically is at the base of the IPCT. From there, the water in the cold water basin is pumped back to the processes served by the tower.

Methods of Determining Emissions

The two types of emissions from cooling towers are evaporative and drift. Evaporative emissions are made up of pure water and possibly volatile contaminants. Drift emissions are water droplets containing dissolved and suspended solids. Drift droplets have the same water chemistry as the water circulating through the tower. Water treatment additives contain anti-corrosion, anti-scaling, anti-fouling, and biocidal additives which can create emissions of VOCs, particulate matter, and toxic compounds. If an industrial process leaks into, or direct contact cooling contaminates the cooling water, these contaminants can be emitted either as volatilized gas, or dissolved and suspended in water drift droplets. Cooling towers can scrub particulates from ambient air, contaminating the cooling water.

For contamination calculations, each will best be done on an individual basis, using process specific knowledge of chemical exposure potential, tower water analysis, and material balances done using best engineering judgment. EPA emission factors can be used as guidelines, but process specific analyses are better.

Particulates are the traditional cooling tower emission measured. Emissions of cooling water treatment chemicals in "drift" can create salting near the tower and PM10 emissions. Particulate and drift emissions can be estimated using AP-42, Chapter 13.4 emission factors.

The NESHAP for Industrial Process Cooling Towers (FR 94-21957) eliminated the use of chromium-based water treatment chemicals for IPCTs that are a major source, or an integral part of a larger major source. Chromium in the +6 valence, a toxic air pollutant, was used in these treatment systems. Phosphate and polymeric dispersant based water treatment chemicals are a typical alternative. Molybdates and zinc are also used. The NESHAP discourages smaller area source IPCTs from using chromium-based water treatment systems through record-keeping requirements.

Biocides are added to cooling towers to inhibit biological growth. Washington State IPCTs have reported chlorine, bleach, and bromine usage. Other biocide systems are probably used also.

Water treatment systems are continually being improved, and system chemistries are often kept confidential by the supplier. For permitting purposes, a supplier will usually divulge the chemistry, but often will label it confidential.

References

Air and Waste Management Association. *Air Pollution Engineering Manual*. New York: Van Nostrand Rienhold, 1992.

Code of Federal Regulations, 40CFR 63 Subpart Q.

National Emission Standards for Hazardous Air Pollutants for Industrial Process Cooling Towers, Federal Register (FR) Doc. No. 94-21957, September 8, 1994.

Prohibition of Hexavalent Chromium Chemicals in Comfort Cooling Towers, Federal Register, 55 FR 222, January 3, 1990.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources,* Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 13.4 Wet Cooling Towers, January 1995.)
(available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

U.S. Environmental Protection Agency. *Methodologies for Estimating Air Emissions from Three Non-Traditional Source Categories: Oil Spills, Petroleum Vessel Loading and Unloading, and Cooling Towers*, June 1993, EPA/600/SR-93/063.

Dry Cleaning

Dry cleaners are the most significant emission source of perchloroethylene in the United States. Figure 1 shows the number of dry cleaners in Washington State by SIC code from one source. However, there is believed to be approximately 800 commercial dry cleaners in Washington (Brady). The largest toxic emissions from dry cleaners are perchloroethylene, trichlorofluoroethane, and petroleum solvents.

Figure 1. Number of Dry Cleaners in Washington State by SIC Code

(Ecology, 1/20/98)

SIC Code	SIC Description	No. of Sources
7215	Coin-operated	37
7216	Commercial	402
7218	Industrial	7

Washington State Department of Ecology has published the *Dry Cleaning Reference Manual* that is useful for complying with state and federal regulations.

Description of Process

The dry cleaning industry consists of coin-operated (Standard Industrial Classification (SIC) Code 7215), commercial (SIC 7216), and industrial sectors (SIC 7218). Coin-operated cleaners use only synthetic solvents and are generally small (about 3.6 to 11.5 kg capacity). Commercial cleaners are larger (14-27 kg capacity) and can use synthetic or petroleum solvents. Industrial cleaners are the largest (230 kg capacity) and about 50% of them use perchloroethylene. (*AP-42*[1], 4.1-1)

The basic steps in dry cleaning are washing, spinning, and drying. The two types of machines used for this process are transfer and dry-to-dry machines. A transfer machine is one in which the washing and drying takes place in different machines and a dry-to-dry machine is one in which the washing and drying takes place in one machine.

The chemicals used for cleaning are either petroleum solvents or synthetic solvents. Petroleum solvents are inexpensive combustible hydrocarbon mixtures and can be used in dry-to-dry and transfer machines. The most common petroleum solvents used in cleaning is the Stoddard solvent (mineral spirits) and 140-F. Synthetic solvents are nonflammable more expensive halogenated hydrocarbons. The two synthetic solvents used today are perchloroethylene (perc), trichlorotrifluoroethane (CFC-113), and 1,1,1-trichloroethane (TCA). Perc plants use transfer and/or dry-to-dry machines and fluorocarbon plants use dry-to-dry machines. Perc is the most common synthetic solvent used, as CFC-113 and TCA are used mostly in specialty cleaning operations. (*AP-42*, 4.1-1)

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[1] U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, October 1997, Document No. AP-42.

For synthetic cleaners the garments are first washed in “charged” solvent which is used solvent with a small portion of detergent for better cleaning. Then the garment is rinsed in pure solvent and is sent to the dryer. The solvent is filtered and part is returned to be used as “charged” solvent. The other portion is distilled to remove oils, fats, greases, and then used in the pure solvent tank. The solids (muck) are removed from the filters once per day and are usually cooked to remove more solvent. The vapors are sent to a refrigerated condenser and separator to recover the solvent. In older perc plants the vapor stream may be sent to a carbon adsorption system to recover the perc instead of a refrigerated condenser, and in fluorocarbon plants the stream can be sent to an unvented refrigeration system. The emissions from the dryer are also sent through similar control devices. (*AP-42*, 4.1-3)

Petroleum plants are the same as synthetic cleaners except in the transfer machines the solvents are removed by spin-drying. Some plants don’t bother to recover the solvent, however, some use water-cooled condensers to recover solvent. There are no control devices for petroleum plants, but emissions can be reduced by maintaining equipment and using good operating practices. (*AP-42*, 4.1-1)

The major toxic emission from a dry cleaning facility is the solvent used and emissions come from all units.

Methods of Determining Emissions

Coin-operated and commercial dry cleaners are usually considered area sources. Industrial dry cleaners are usually considered point sources. The commercial dry cleaner category produces the most emissions.

Perc, CFC-113, and TCA are not considered photochemically reactive, therefore, they do not contribute to tropospheric ozone formation and should not be included in an VOC inventory. However, perc and TCA (listed as methyl chloroform in Washington Administrative Codes (WAC) 173-460) are air toxics and should be included in a toxics inventory. CFC-113 is not listed as an air toxic in Washington State regulations, but may be listed in other states as an air toxic. TCA and CFC-113 are also stratospheric ozone-depleting substances. (EIIP, 4.2-2)

For determining emissions from a specific dry cleaner, the best method is material balance for the solvent used.

EIIP (pg. 4.3-1) recommends other methods for determining emissions over large areas summarized below:

> “Number of facilities or dry cleaning units:
> - Local per facility emission factors (using survey or permit information)
> - Emission factors based on type of machine
> - National average per facility emission factors
>
> Number of employees:
> - Local per employee emission factors (using survey or permit information)
> - National average per employee emission factors
>
> Per capita:
> - National average per capita emission factor”

The document goes into detail about how to apply these methods to different dry cleaner operations.

For determining emissions over large areas for coin-operated and commercial cleaners it is best to establish local emission factors using a survey (detailed in EIIP, 4.4-1). The dry cleaning NESHAP requires all those facilities using perc to report a description of their dry cleaning machine and the amount of perc used to their EPA Regional Office, therefore a survey may not be necessary. However, if developing local emission factors is not practical, national emission factors are available in AP-42 on a kg per kg of garments washed basis and also on a per capita basis.

References

Brady, Bernard. Washington State Department of Ecology, Personal Communication.

Emission Inventory Improvement Program (EIIP): Volume III: Chapter 4: Dry Cleaning, Radian Corporation, May 1996.
(available by chapter on Internet at http://earth1.epa.gov/oar/oaqps/eiip/)

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 4.1, Dry Cleaning, April 1981)
(available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Washington State Department of Ecology, *Controlling Air Toxics: Complying with State Laws*, June 1992, Publication No. 92-51.

Washington State Department of Ecology, *Dry Cleaner Reference Manual: Complying with Washington State and Federal Environmental Regulations*, April 1996, Publication No. 96-200.

Washington State Department of Ecology, *Facility/Site on the Web*, accessed 1/20/98.
(http://www.wa.gov/ecology/iss/fsweb/fshome.html)

Fertilizer Plants

Fertilizer is used to amend soils to promote the growth of desirable plants. The main components of fertilizer are nitrogen, phosphorous, and potassium. There are other elements, such as iron and sulfur, that are important to the vigorous growth of plants but they are needed in much lower concentrations and are generally available in the native soil. In Washington, chemical fertilizers are produced by a combination of large fixed facilities. They produce nitric acid and ammonia to react with each other, with phosphates, and with other elements and smaller mobile facilities that generate ammonium phosphate. There are also a limited number of facilities that process metal fume to produce blends of trace elements of soil amendments.

There are four distinct types of fertilizers:
- ammonium nitrate
- normal superphosphate
- triple superphosphate (TSP):
  - Run Of the Pile (ROP)
  - Granular Triple Superphosphate (GTSP)
- ammonium phosphate

Phosphorus pentoxide (P2O5) is used to measure the phosphorous content of fertilizer.

In Washington, there are approximately 14 facilities that fall under SIC code 2873 Nitrogenous Fertilizers and 2 facilities that fall under SIC code 2874 Phosphate Fertilizers (Ecology, 1/20/98).

In 1996 the 54th Legislature passed Substitute House Bill 2338 on March 1, 1996. Chapter 70.94 RCW will be amended to state that the Department of Ecology will not regulate ammonia emissions resulting from the storage, distribution, transportation, or application of ammonia for use as an agricultural fertilizer. Manufacturing of ammonia based products are still subject to regulation.

Description of Process

Ammonium Nitrate Fertilizer

Approximately 60 percent of the ammonium nitrate produced in the U.S. is sold as a solid product. To produce a solid product, the ammonium nitrate solution is concentrated in an evaporator or concentrator. The resulting "melt" contains about 95 to 99.8 percent ammonium nitrate at approximately 300°F. This melt is then used to make solid ammonium nitrate products.

The manufacture of ammonium nitrate involves several unit operations including solution formation and concentration; solids formation, finishing, screening and coating; and product bagging and/or bulk shipping. All ammonium nitrate plants produce an aqueous ammonium nitrate solution through the reaction of ammonia and nitric acid in a neutralizer. In some cases, solutions may be blended for marketing as liquid fertilizers.

The number of operating steps employed depends on the end product desired. For example, plants producing ammonium nitrate solutions alone use only the solution formation, solution blending and bulk shipping operations. Plants producing a solid ammonium nitrate product may employ all of the operations. (*AP-42*[1], Section 8.3)

There are several 10-34-0 (10% nitrogen, 34% phosphorus pentoxide and 0% potassium) granulators and generators in this state. They include portable and permanent generators.

Normal Superphosphate Fertilizer

Normal superphosphate fertilizer contains between 15 and 21 percent P_2O_5. It is manufactured by reacting ground phosphate rock with 65 to 75 percent sulfuric acid. This is described by the following equation: (U.S. EPA, May 1979)

$$[Ca_3(PO_4)_2]_3CaF_2 + 7H_2SO_4 + 3H_2O \rightarrow 3[CaH_4(PO_4)_2.H_2O] + 7CaSO_4 + 2HF$$

Fluorapate (phosphate rock) + sulfuric acid + water ➜ mono-calcium phosphate monohydrate + calcium sulfate + hydrogen fluoride

Chapter 40 C.F.R., Part 60, Subpart U regulates the standards of performance for the phosphate fertilizer industry. The Standard Industrial Code (SIC) for normal superphosphate fertilizer is 2874.

Triple Superphosphate Fertilizer

Triple superphosphate fertilizer contains greater than 40 percent P_2O_5. There are two processes Run Of the Pile Triple Superphospate (ROP-TSP) and Granular Triple Superphosphate (GTSP). Chapter 40 C.F.R., Part 60, Subpart W regulates the superphosphoric acid plants.

Ammonium Phosphate Fertilizer

Ammonium phosphate fertilizer is either in granular or liquid form. Granular ammonium phosphate ($NH_4H_2PO_4$) is produced by reacting phosphoric acid (H_3PO_4) with anhydrous ammonia (NH_3). Ammoniated superphosphates are produced by adding normal superphosphate or triple superphosphate to the mixture. (*AP-42*, Section 8.5)

For liquid 10-34-0 fertilizer production, ammonia and superphosphoric acid are reacted in an inverted U-tube reactor creating temperatures in excess of 600°F. Water is added and the product is cooled and stored prior to application. (Ryan, June 18, 1992) For portable units, the stack is limited to 13.5 feet so that it may travel under bridges and overpasses.

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[1] U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, October 1997, Document No. AP-42.

Methods of Determining Emissions

EPA's SPECIATE database has identified the following toxic pollutant emissions from normal superphosphate and triple superphosphate production: hexane, methyl alcohol, formaldehyde, methyl ethyl ketone, benzene, toluene, and styrene (*AP-42*).

Several stack test for toxic emissions have been performed in the U.S., please see references for details.

Emissions factors are available in *AP-42* for particulate matter. There are also emissions factors for ammonia for ammonium nitrate production, and for fluoride and ammonia for ammonium phosphate production.

References

Centex/Land O'Lakes Agronomy Company, *Letter Report to Greg Ryan transmitting the Emissions and Compliance Study*, July 27, 1994.

Johnson, Karl T., *Letter to Mr. Chris Myrick discussing states regulatory levels,* The Fertilizer Institute, January 12, 1993.

NIOSH Pocket Guide to Chemical Hazards, U.S. Department of Health and Human Services, Public Health Services Center for Disease Control, National Institute for Occupational Safety and Health, September 1985, U.S. Government Printing Office, Washington D.C. 20402.

Ryan, Greg, *Memo to Myron Saikewicz on 10-34-0 Fertilizer Plants*, Washington State Department of Ecology, June 18, 1992.

Tennessee Valley Authority, *Production of Ammonium Polyphosphate Solutions from Wet-Process Superphosphoric Acid,* March 21, 1974, TV40218A, El Dorado, Kansas.

Tennessee Valley Authority, *Results of Stack Gas Sampling for Mears Fertilizer Company, Inc*, September 9-10, 1991. Chemical Development Department, National Fertilizer and Environmental Research Center, Muscle Shoals, Alabama.

U.S. Environmental Protection Agency, *Source Assessment: Phosphate Fertilizer Industry*, May 1979, EPA-600/2-79-019C. Office of Research and Development, Research Triangle Park, NC.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, , January 1995, Document No. AP-42. (Section 8.3 Ammonium Nitrate, Section 8.5, Phosphate Fertilizers, July 1993). (available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Washington State Department of Ecology, *Facility/Site on the Web*, accessed 1/20/98. (http://www.wa.gov/ecology/iss/fsweb/fshome.html)

Fiberglass Production

The fiberglass reinforced plastics industry in Washington produces a range of products including boats, auto and truck canopies, aircraft parts, corrosion resistant tanks and piping, shower stalls, bathtubs, spas, marbled products, and a variety of specialty items from skis to sail boards.

There were 55 fiberglass resin product businesses in Washington that were large enough to be involved in the Pollution Prevention Planning program, but over 1,000 businesses were listed in associated Standard Industrial Classification (SIC) codes. The largest single category in Washington is boat builders. Other SIC codes with known fiberglass resin product businesses in Washington are listed in Figure 1 with the number of facilities in Washington. The pollution prevention plans and yearly updates give good insight into each plant's processes, raw material usage, and pollution prevention activities with accompanying reduction trends of emissions.

Fiberglass Manufacturing
Figure 1. Standard Industrial Classification (SIC) Codes in WA State
(Ecology, 1/20/98)

SIC	SIC Description	No. of Facilities
3081	Unsupported plastics film and sheets	7
3084	Plastic Pipe	14
3088	Plastics plumbing fixtures	11
3089	Plastics products, nec	67
3433	Heating equipment, except electric	5
3713	Truck and bus bodies	21
3728	Aircraft Parts and Equipment	99
3732	Boat building and repairing	228
3949	Sporting and athletic goods, nec	32

Description of Process

The most common method of reinforced plastics production is open molding. Boat manufacturing is typical and will be used as an example. First the surface of the mold is polished and coated with a wax, which allows easy removal of the finished product from the mold after curing. Next gel coat, consisting of unsaturated polyester resin, catalyst, and pigments, is sprayed onto the waxed mold. This forms the outer, visible surface of the boat.

After the gelcoat is fully cured, fiberglass reinforcing material saturated with catalyzed polyester resin is applied over it. Methods of application are: (1) chopper gun (spray coat) - the resin, catalyst and fiberglass strand are fed into a gun, and the fiberglass is chopped into short segments and sprayed with the resin into the mold; (2) hand layup - the resin is catalyzed, then brushed on to layers of glass mat or roving which have been hand fitted into or over the mold. Air bubbles and other imperfections are removed by rollers, by hand. Tools are cleaned periodically of resin, using acetone or a substitute cleaner before the resin begins to polymerize.

After the lay-up is cured, it is trimmed, removed from the mold, and manufactured into a boat or other finished product.

Methods of Determining Emissions

Air emissions data on the fiberglass resin product industry in Washington state is available from the Washington Emissions Data System (WEDS), Toxic Release Inventory (TRI), and the Pollution Prevention Planning effort of Ecology's Hazardous Waste and Toxics Reduction Program. National emissions estimates are also available from EPA.

Total national VOC emissions from fiberglass boat manufacturing are estimated to be 20,150 tons per year (U.S. EPA, May 1990). Approximately, 64 % of these emissions are styrene, resulting from gel coating and lamination; the remainder is acetone or some other solvent used during clean-up.

There are four primary areas in the fiberglass boat production processes where VOC may be emitted to the atmosphere. These are resin storage, the production area, the assembly area, and waste disposal. The major emission sources are exhausts from gel coat spray booths, room exhausts from the lamination area, and evaporation of acetone or other solvents during clean-up. Styrene emissions occur during the lamination of the deck, hull, and small parts, due to evaporation from the resin or gel coat over-spray and from vaporization from the applied resin or gel coat before polymerization occurs.

Emissions should be calculated using actual resin monomer contents. When specific information about the percentage of styrene is unavailable, the representative average values in *AP-42's*[1] Table 4.12-3 should be used. The sample calculation illustrates the application of the emission factors.

Parameters needed for estimating styrene emissions will be:
- process type to choose appropriate emission factor.
- resin quantity used
- resin monomer type, percent, and whether vapor stabilized or not

Acetone and other solvent emissions should be estimated using:
- amount of solvent purchased
- solvent sent offsite (disposal, recycling, etc.)
- any other appropriate material balance considerations

> <u>Sample Calculation</u> A fiberglass boat building facility consumes an average of 250 kg per day of styrene-containing resins using a combination of hand layup (75%) and spray layup (25%) techniques. The laminating resins for hand and spray lay up contain 41.0 and 42.5 weight percent, respectively, of styrene. The resin used for hand layup contains a vapor-suppressing agent.

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[1] U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, October 1997, Document No. AP-42.

From Table 4.12-2 of AP-42 the factor for hand layup using a vapor suppressed resin is 2 - 7 (0.02 to 0.07 fraction of total styrene emitted); the factor for spray layup is 9 - 13 (0.09 to 0.13 fraction emitted). Assume the midpoints of these emission factor ranges.

Total VOC emissions are:
(250 kg/day) [(0.41)(0.045)(0.75) + (0.425)(0.11)(0.25)] = 6.4 kg/day.

Emissions from use of gel coat would be calculated in the same manner. If the monomer content of the resins were unknown, a representative value of 43 percent could be selected from Table 4.12-3 for this process combination. It should be noted that these emissions represent evaporation of styrene monomer only, and not of acetone or other solvents used for cleanup.

Another source of emission factors is from a masters thesis study that Stacia Dugan and Dr. Michael Pilat of the University of Washington did on styrene emissions from Philips/Hytec (now called Lasco Products) in Yelm, Washington in August, 1990. Philips/Hytec manufactures fiberglass tubs and showers. It is left up to the reader whether they represent valid emission factors. They imply that from 30 to 65 percent of the styrene in the various resins is emitted to the air during processing.

The EPA, National Marine Manufacturing Association, and the Composites Manufacturing Association are currently (1998) sponsoring and evaluating additional testing to update styrene emission factors. These tests will probably bring a revision to the current AP-42 emission factors, which will probably result in an increase in emission factors.

Acetone and other volatile solvents are almost all emitted to the air, so the emission factor for volatile cleaning solvents is essentially 1.0. A material balance between purchased acetone and any acetone in wastes sent offsite will be the best estimate of air emissions. Other solvent usage can be done similarly.

The Puget Sound Air Pollution Control Authority (PSAPCA) Regulation II, Section 3.08 Polyester, Vinylester, Gelcoat, and Resin Operations (revised 12/09/93) requires fiberglass resin product businesses to register with the agency, and use an enclosed, vented spray area. It also sets spray gun specifications, and sets controls on volatile clean-up solvents.

One of two federal National Emission Standards for Hazardous Air Pollutants (NESHAP) will be applicable to fiberglass manufacturers that emit more than 10 tons of styrene into the air. Boat manufacturers will be covered under the Fiberglass Boat Manufacturing NESHAP, and all other fiberglass manufacturers will be covered by the Fiberglass Reinforced Plastics Composites NESHAP. Both federal rules are due in proposed form in 1999, and final rule in 2000. The EPA contact is Madeleine Strum at (919) 541-2383 or e-mail at strum.madeleine@epamail.epa.gov. Bob Burmark (Ecology) and Bob Goldberg (Ecology) are participating with the EPA, states, and the fiberglass industry to develop these federal rules.

Fiberglass manufacturers that emit less than 10 tons per year of styrene will not be subject to these NESHAPs, but are subject to all other applicable federal, state, and local regulations.

It is projected that several fiberglass manufacturers in Washington will be permittable due to styrene emissions greater than ten tons. Acetone is exempt from federal and state VOC reporting because it has a negligible contribution to ozone formation.

References

U.S. Environmental Protection Agency, *Assessment of VOC Emissions from Fiberglass Boat Manufacturing*, May 1990, EPA-600/2-90-019. EPA's Control Technology Center at Research Triangle Park, NC, Charles H. Darvin Project Officer.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 4.12, Polyester Resin Plastics Product Fabrication, September, 1988) (available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Washington State Department of Ecology, *Facility/Site on the Web*, accessed 1/20/98. (http://www.wa.gov/ecology/iss/fsweb/fshome.html)

Washington State Department of Ecology, *Pollution prevention planning annual reports and yearly updates*. Available from the Ecology Regional Offices. Ecology statewide fiberglass resin product contact: Bob Goldberg @ (360)407-6350.

Washington State Department of Ecology, *Washington Emissions Data System (WEDS)*, Contact: Sally Otterson, 360-407-6806.

Washington State Department of Ecology, *Washington State Toxic Release Inventory*, *Summary Report: 1991 and 1992*. Publication no. 94-91A and 94-91B.

Ink and Paint Manufacture

In Washington State there are about 47 companies manufacturing paint (SIC 2851), and about 12 manufacturing printing ink (SIC 2893) (Ecology, 1/20/98). Paint and ink manufacturing are grouped together because their manufacturing processes have a lot of similarities. Nationally, paint and ink manufacturing contributes an estimated 0.05% of total volatile organic compound (VOC) emissions. The application of these paints and inks accounts for an additional 13% of VOC emissions. (U.S. EPA, 1992)

Description of Process

The products of the paint manufacturing industry include architectural coatings, product coatings for original equipment manufacturers (OEM), and special-purpose coatings. The four primary types of inks are letterpress inks, lithographic and offset inks, gravure inks, and flexographic inks. All of these products are made with the same basic raw materials: pigments, solvents, resins (or binders), and other additives. In most cases, the manufacturing facilities purchase those raw materials and then formulate or blend, rather than react, to produce a finished product.

The batch process production of paint and ink involves four major steps:
I. Preassembly and premix
II. Pigment grinding/milling
III. Product finishing/blending
IV. Product filling/packaging

Some of the equipment used to accomplish these manufacturing steps include roller mills; ball and pebble mills; attritors; sand, bead, and shot mills; horizontal media mills; and high-speed disk dispersers. (U.S. EPA, 1992)

Methods of Determining Emissions

Paint Manufacturing

Paints are either solvent or water based. Most plants produce both. Solvent based paints are the source of most plant VOCs, but water based paint formulations do include VOCs. Mixing in open top drums and portable tanks (sized from 50 to 3,000 gallons) causes fugitive emissions. Lids are usually used, but fugitive evaporative emissions still occur when lids are open, through mixer openings or cracks, and when filling or emptying. Product packaging and equipment cleaning create emissions. Solvent storage tanks vent emissions when being filled, from day/night heating/cooling, or from simple diffusion.

Toxic emissions from Washington paint manufacturers may include xylene, toluene, methyl ethyl ketone, methyl isobutyl ketone, methanol, isopropyl alcohol, acetone, n-butyl acetate, ethyl acetate, iso-butane, methyl chloroform, and methylene chloride.

Information for emission estimates can be found in *AP-42*[1] and from the National Paint and Coatings Association.

Ink Manufacturing

Letterpress and lithographic inks are thick and viscous (paste-like). Gravure and flexographic inks are fluid and utilize a much lower viscosity vehicle. The letterpress inks and lithographic inks dry by oxidation (and polymerization) of the vehicle, or vehicle absorption into the printing surface, while fluid inks dry by solvent evaporation.

Many of the ink manufacturers are responding to pollution prevention pressures by formulating new inks based on low VOC vehicles like soy or other vegetable oils. Water-based formulations reduce VOCs quite a bit, but they still use some volatile solvents. Inks can be blended in quantities from 1 pound to several thousand gallons.

Washington ink manufacturers blend and formulate, but a cursory search has not found any that cook ink vehicles. (Grahm) If an ink manufacturer cooks an ink vehicle to make varnish, this can create VOC emissions of 40 - 160 pounds per ton vehicle cooked, which would probably be the plant's major source of VOCs. Most Washington ink manufacturers purchase pre-cooked vehicles if they need them for ink formulations.

All emission estimation methods need data on solvent purchases and usage, including the solvent type, pounds per year used in each usage, and MSDS or manufacturer's formulation data on any purchased blended materials (to determine the amount of solvents).

The Puget Sound Air Pollution Control Agency (PSAPCA) has a rule regulating Coatings and Ink Manufacturing. It requires VOC containing mixing vats to be covered, sets lid design and maintenance requirements, and requires solvent clean-up to be done in a manner that minimizes emissions of VOCs. These type of regulations are simple, sensible, and widely used throughout the nation.

Storage tank emissions could be better controlled if pressure/vacuum conservation vents and submerged fill pipe or bottom fill tanks were required, but this looks like a small HAP source at these plants.

Limits on VOC contents of specialty coatings, architectural coatings, and inks are lowering VOC emissions from manufacturing facilities. Whether these limits are placed by regulatory agencies, or the result of market forces driven by pollution prevention activities, product reformulation and substitution of lower VOC alternative products will be a strong future driving force to lower VOC emissions from both application and manufacturing of paints and inks.

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[1] U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, October 1997, Document No. AP-42.

References

Buonicore, Anthony J. and Wayne T. Davis. *Air Pollution Engineering Manual*, Air & Waste Management Association, VanNostrand Reinhold, New York, 1992, pp. 451-456.

Grahm, Andy, INX International, Seattle, WA. Personal communication.

Lilly, W. Donald, Vice-President, Quality Control & Environmental Management, United Coatings, Greenacres, WA. Personal communication.

National Paint & Coatings Association, *Emission Estimation Guidance Manual for the Paint and Coatings Industry*.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 5.10, Paint and Varnish and Section 5.14 Printing Ink; May 1983). (available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

U.S. Environmental Protection Agency, *Control of VOC emissions from Ink and Paint Manufacturing Processes*, April 1992, EPA-450/3-92-013.

Washington State Department of Ecology, *Facility/Site on the Web*, accessed 1/20/98. (http://www.wa.gov/ecology/iss/fsweb/fshome.html)

Municipal Waste Landfills

There are approximately 340 facilities in Washington under SIC code 4953 Refuse Systems (Ecology, 1/20/98). Besides landfills this could include incinerators and waste treatment plants.

Research data for municipal waste landfills is mostly oriented around methane generation rates and biology. There has been source testing done to evaluate what other compounds can be emitted from landfills. EPA, when developing the background document for the 40 CFR 60, Subpart WWW, reviewed the available data and evaluated the available emission models. Based on the source test data, EPA selected 12 organic compounds that showed up in essentially all the landfills for which data was reported. Of the chemicals reported and included in EPA's list, vinyl chloride is the most problematic. Vinyl chloride is not only present in the solid waste; it is also a byproduct of the biodegradation of other chlorinated compounds.

Methods of Determining Emissions

The emission controls that are available for use on landfill gas emissions are elevated burners (“tiki torches”), ground burners, various regenerative incinerators, conversion to methanol and hydrogen, internal combustion engines, gas turbines, and cleaning to pipeline-quality gas for sale.

All of these control methods result in a reduction of methane and other toxic and non-toxic hydrocarbons that are emitted in the landfill gases. All of them require that the landfill gases be collected and piped to one or more centralized control devices. At this time, no effective biological control methods have yet been devised.

The conversion of landfill gas from methane to carbon dioxide is encouraged by the international global warming accords and the EPA. Carbon dioxide is a much less potent greenhouse gas than methane. EPA’s global warming initiative has been actively encouraging the installation of energy recovery systems at landfills which generate enough gas to support such systems.

A major concern with landfill emissions is the methane generation rate. Methane and carbon dioxide generated by anaerobic decomposition of wastes is the major means for non-methane organic compounds (NMOCs) to leave the landfill. This rate is dependent on the level of moisture in the landfill and requires a fully anaerobic environment. The bacteria that co-metabolize the various chlorinated compounds in the waste are often obligate anaerobes also. Early emissions of many chemicals from the landfill are dominated by volatilization of the chemical from the waste. Later, some of these chemicals are generated as by-products of the metabolization of more complex compounds. Vinyl chloride is emitted both from volatilization of vinyl chloride contained in the solid waste and as a result of degradation of trichloroethene and dichloroethene. It also appears that lignin (from woody yard waste) is degraded to a variety of aromatic compounds, eventually forming benzene, toluene, phenols, alcohols and esters. (U.S. EPA, 1991).

Emission controls that provide for 98% NMOC control may still have vinyl chloride emissions that exceed the ASIL, depending on the distance from the fill to the fenceline.

The recommendation for estimating uncontrolled landfill emissions is to use EPA's Landfill2 model (which predicts emissions for 50 years after landfill is full). If the landfill specific rate parameters have not been determined, the landfill regulation requires the use of the parameters in the most recent version of *AP-42*[1].

All of these factors reflect a national average. Many of the landfills used to establish this average are located in arid areas. The “old” factors were based on the worst case emissions from 931 landfills nationwide. The revised values used in the most recent version of the draft regulation and in AP-42 include many more landfills or more tests on specific landfills (58 FR 117).

All of these parameters can be determined experimentally at the landfill, as can specific compound concentrations. EPA has finalized and published testing and analysis methods for these factors (RM 304A and RM 304B, Biodegradation rate, RM 25C, Determination of Nonmethane Organic compounds (NMOC) in MSW Landfill gases, issued and RM 2E, Flow rate from landfill wells).

The uncontrolled emission rates produced by the Landfill2 model should then be adjusted to account for the control efficiency of controls installed.

To estimate landfill emissions using the Landfill2 model, the minimum information needed is the surface area (square meters), maximum depth (meters), average depth (meters), landfill volume (megagrams), year landfill began accepting waste, and the k & L_o factors given in AP-42. Table 1 gives a summary of non-methane organic compounds found in landfill gas.

Solid waste is normally compacted after being placed in the landfill. Normal compaction results in an in-place density of 500 to 1500 lb./cu.yd. An average compaction factor is in the range of 700-900 lb./cu.yd. Most landfills of smaller size (300,000 cu.yd. or smaller) not having a known density or weight of waste received will best be modeled with a conversion of 700 lb./yd. This lower value is due to the smaller size machinery used at these fills which results in a lower level of compaction. The highest level of compaction will be the result of the use of heavy equipment for compacting the waste and/or the use of compacted and baled waste (bale fills). Larger landfills will usually have scales to weigh the incoming waste so a means to convert material volume to compacted weight is not needed.

Bale fills have very high waste densities due to compressing the waste. They exhibit high weight per volume and low gas and liquid porosities. The literature does not indicate whether anyone has determined k and L_o values for a balefill. The best that can be said for balefills is that they will become anaerobic faster once there is adequate moisture in the fill, but it will take longer for that moisture to get into the fill.

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[1] U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources,* Fifth Edition with Supplements, October 1997, Document No. AP-42.

References

Code of Federal Regulations, 40 CFR 60, Subpart WWW-Standards of Performance for Municipal Solid Waste Landfills.

Federal Register, 58 FR 117, June 21, 1993, pp. 33790-33792.

U.S. Environmental Protection Agency, *Background Information Document for Air Emissions from Municipal Solid Waste Landfills*, March 1991, EPA-450/3-90-011a, pp. 3-10.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 2.4 Municipal Solid Waste Landfills, September 1997.) (available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Washington State Department of Ecology, *Facility/Site on the Web*, accessed 1/20/98. (http://www.wa.gov/ecology/iss/fsweb/fshome.html)

Table 1. Summary of Non-Methane Organic Compounds Found In Landfill Gas **(U.S. EPA, 1991)**

Chemical Name	**No. of Times Quantified**	**Average Conc. ppm**	**Average Conc. Detected ppm**	**Highest Conc. ppm**	**Lowest Conc. ppm**
Ethane	26	142.79	252.63	1780	0
Toluene	40	51.60	59.34	758	0.2
Methylene chloride	37	19.70	24.5	174	0
Hydrogen sulfide	3	16.50	252.97	700	11
Ethylbenzene	31	14.64	21.73	428	0.15
Xylene	2	14.52	333.85	664	3.7
1,2-Dimethyl benzene	1	12.78	588	588	588
Limonene	1	10.22	470	470	470
Total xylene isomers	27	10.04	17.11	70.9	0
Alpha-pinene	1	9.70	446	446	446
Dichlorodifluoromethane	31	8.83	13.1	43.99	0
Etylester butanoic acid	1	8.65	398	398	398
Propane	26	7.68	13.59	86.5	0
Tetrachloroethene	39	7.15	8.43	77	0
Vinyl chloride	42	7.04	7.71	48.1	0
Methylester butanoic acid	1	6.63	305	305	305
Ethylester acetic acid	1	6.13	282	282	282
Propylester butanoic acid	1	5.50	253	253	253
1,2-Dichloroethene	37	5.09	6.33	84.7	0
Methyl ethyl ketone	27	4.80	8.17	57.5	0
Thiobismethane	1	4.57	210	210	210
Methlycyclohexane	2	4.33	99.7	197	2.4
Trichloroethene	44	3.80	3.98	34	0.01
Nonane.	1	3.63	167	167	167
Benzene	45	3.52	3.6	52.2	0
Ethanol	1	3.41	157	157	157
Acetone	26	3.36	5.94	32	0
2-Butanol	1	3.30	152	152	152
Octane	1	3.30	152	152	152
Pentane	26	3.19	5.64	46.53	0
Hexane	26	3.01	5.33	25	0
Methylester acetic acid	1	2.96	136	136	136

Chemical Name	No. of Times Quantified	Average Conc. ppm	Average Conc. Detected ppm	Highest Conc. ppm	Lowest Conc. ppm
1-Methoxy-2-methyl propane	1	2.96	136	136	136
2-Butanone	1	2.80	129	129	129
1,1-Dichloroethane	3	2.52	3.51	19.5	0
1-Butanol	1	2.17	100	100	100
Butane	26	2.08	3.68	32	0
4-Methyl-2-pentanone	1	1.93	89	89	89
2-methyl propane	1	1.83	84	84	84
1-methylethylester butanoic acid	1	1.50	69	69	69
2-methyl methylester propanoic acid	1	1.50	69	69	69
Carbon tetrachloride	37	1.49	1.85	68.3	0
Chloroethane	29	1.28	2.03	9.2	0
1,1,3-Trimethyl cyclohexane	1	1.24	57	57	57
2-Methyl-1-propanol	1	1.11	51	51	51
1,2-Dichloroethane	37	1.05	1.3	30.1	0
Trichlorofluoromethane	46	0.99	0.99	11.9	0
Chloromethane	30	0.90	1.38	10.22	0
2,5-Dimethyl furan	1	0.89	41	41	41
2-Methyl furan	1	0.87	40	40	40
Chlorodifluoromethane	27	0.79	1.35	12.58	0
Propene	1	0.78	36	36	36
Methyl isobutyl ketone	26	0.78	1.38	11.5	0
Ethyl mercaptan	3	0.78	11.93	23.8	1
Dichlorofluoromethane	28	0.73	1.2	36.11	0
1,1,1-Trichloroethane	38	0.69	0.84	9	0
Tetrahydrofuran	1	0.65	30	30	30
Ethylester propanoic acid	1	0.57	26	26	26
Bromodichloromethane	29	0.45	0.71	7.85	0
Ethyl acetate	1	0.43	20	20	20
3-Methylhexane	1	0.43	20	20	20
ClOH16 unsaturated hydrocarbon	1	0.33	15	15	15
Methylpropane	1	0.26	12	12	12
Chlorobenzene	29	0.24	0.38	10	0
Acrylonitrile	26	0.18	0.32	7.4	0
Methylethylpropanoate	1	0.16	7.3	7.3	7.3

Chemical Name	No. of Times Quantified	Average Conc. ppm	Average Conc. Detected ppm	Highest Conc. ppm	Lowest Conc. ppm
1,1-Dichloroethene	32	0.16	0.23	3.1	0
Methyl mercaptan	3	0.12	1.87	3.3	1
1,2-Dichloropropane	28	0.07	.012	1.8	0
i-propyl mercaptan	2	0.07	1.55	2.1	1
Chloroform	36	0.06	0.08	1.56	0
1,1,2,2-Tetrachloroethane	28	0.06	0.1	2.35	0
1,1,2,2-Tetrachloroethene	2	0.06	1.33	2.6	0.05
2-Chloroethylvinyl ether	28	0.05	0.08	2.25	0
t-butyl mercaptan	2	0.03	0.64	1	0.28
Dimethyl sulfide	2	0.02	0.55	1	0.1
Dichlorotetrafluoroethane	1	0.02	1.1	1.1	1.1
Dimethyl disulfide	2	0.02	0.55	1	0.1
Carbonyl sulfide	1	0.02	1	1	1
1,1,2-Trichloro-1,2,2-trifluoroethane	1	0.01	0.5	0.5	0.5
Methyl ethyl sulfide	1	0.01	0.32	0.32	0
1,1,2-Trichloroethane	28	0.00	0	0.1	0
1,3-Bromochloropropane	1	0.00	0.01	0.01	0.01
1,2-Dibromoethane	2	0.00	0	0	0
C-1,3-Dichloropropene	2	0.00	0	0	0
T-1,3-Dichloropropene	2	0.00	0	0	0
Acrolein	26	0.00	0	0	0
1,4-Dichlorobenzene	28	0.00	0	0	0
Bromoform	28	0.00	0	0	0
1,3-Dichloropropane	26	0.00	0	0	0
1,2-Dichlorobenzene	29	0.00	0	0	0
1,3-Dichlorbenzene	29	0.00	0	0	0
Dibromochloromethane	28	0.00	0	0	0
Bromomethane	28	0.00	0	0	0

Municipal Wastewater Treatment Plants

There are approximately 351 facilities in Washington under SIC code 4952 Sewerage Systems.

Methods of Determining Emissions

In evaluating the emissions from municipal wastewater treatment plants one factor has become obvious, the quantity of emissions are not large enough to warrant being regulated as a VOC source. It is possible that the emission of a specific compound will exceed its Ambient Source Impact Level (ASIL) (Chapter 173-460 WAC) off of the plant site.

Conditions that may lead to emissions of a toxic air pollutant (TAP) that causes its ASIL to be exceeded are:

- A treatment plant with the secondary treatment unit (aeration basin, trickling filter, etc.) close to the facility property line.
- Any treatment plant receiving water from a chlorinated drinking water supply.
- A treatment plant receiving effluent from one or more industries that are discharging considerable quantities of volatile organic compounds.
- Any industrial wastewater treatment facility.
- Any solid waste disposal site leachate treatment facility.
- Any wastewater treatment plant that uses surface aeration processes.

Emission rates of air pollutants from the wastewater treatment process are not subject to a simple set of estimating factors unless those factors were developed specifically for that facility or a group of related facilities by means of source testing. Because of the variability of the design of the process components, drinking water quality, wastewater temperature and inorganic chemical content, and waste characteristics, a simple emission factor based on the influent flow rate or some such factor is not appropriate.

There have been several studies done recently on air emissions from sewage treatment plants. The largest study was required by the South Coast Air Quality Management District for all wastewater treatment facilities in their jurisdiction. This study looked only at total reactive organic gas emissions, not the individual compounds. This study was called Joint Emission Inventory Program and resulted in a set of unit process specific emission factors for ROG. This set of factors is called Pooled Emission Estimating Program. When applied to the plants for which these factors were developed, they are not very 'conservative' in that they are very close to the actual emission rate rather than being relatively conservative, higher than actual, as appropriate for a regulatory basis. The basic PEEP report does have emission factors for individual compounds by process unit.

Water Environment Research Foundation (WERF) has funded a multi-year research project that is looking at the emission rates for the 59 most common VOCs found in municipal wastewater treatment plant influents from process units and from various odor control devices in common use.

Table 1 lists some of the available models for estimating emissions from wastewater treatment facilities.

Based on the influent VOC testing by Ecology's Environmental Investigations and Laboratory Services Section, chloroform ($CHCl_3$) is the major pollutant of concern from the treatment process. Chloroform is generated during the chlorination of the water supply and during certain wastewater treatment plant chlorination activities. The chloroform coming in with the wastewater is more significant in terms of air emissions than the chloroform generated at the treatment plant during disinfection and prechlorination processes.

Emissions of volatile compounds from a wastewater treatment plant of any kind occur mostly at those locations where the water surface is turbulent. These areas are primarily aerated grit tanks, aerated channels, aeration basins, clarifier weirs, and other weirs or areas that have high levels of turbulence. Chlorination of the final effluent is not a significant source of chloroform emissions but is a significant source of effluent chloroform which will become air emissions when the chlorinated effluent is spray irrigated for disposal or falls over a water fall.

A typical emission profile from an air activated sludge treatment plant shows that most emissions from a treatment plant occur in the aeration basin of an activated sludge plant. Lower but potentially significant levels of emissions occur at clarifier weirs and aerated grit chambers.

A pure oxygen activated sludge facility has much lower emissions of volatile air contaminants due to the much lower air usage rates and increased ability for biodegradation to occur in the oxygen rich activated sludge tanks. The bulk of the air emissions from this kind of treatment plant come from the primary and secondary clarifiers, headworks and any aerated channels at the facility.

Emissions from a sewage treatment plant are not constant but vary in relation to the flow received by the plant, the timing and content of industrial and commercial discharges to the plant, toxic material spills, the presence of any leaking underground gasoline or chemical storage tanks and, at very large facilities, by certain maintenance and odor control operations like prechlorination, chlorination of clarifier weirs to control algal growths, and by the adding and removing process units from service.

At this time there are no good models to account for the loss of volatile compounds from spray irrigated wastewater. A suggestion on how to model sprayfield emissions is to use

Table 1. Available Models for Estimating Emissions

PROCESS	AP-42	SIMS	TOXCHEM+	FATE	BASTE	Water8	CORAL
Aerated Grit removal	Ok	Ok	Yes	Ok	Yes	Yes	No
Primary clarifiers	Yes	No	Yes	No	Yes	Yes	No
Activated sludge basins	Ok	Ok	Yes	Yes	Yes	Yes	No
Trickling filters, RBC's, biotowers	No	No	Yes	No	Yes	Yes	No
Secondary clarifiers	Yes	No	Yes	No	Yes	Yes	No
Aerated lagoons	Yes	Yes	No*	No	Yes	Yes	No
Facultative lagoons	Yes	Yes	No*	No		Yes	No
Collection system components	Yes	Yes	Yes	No		Yes	Yes
Haz. waste lagoons	Yes	Yes	No	No			No
Spray irrigation	No	No	No	No			No
Evaporative lagoons	Yes	Yes	No	No			No

* The model can be made to mimic these processes

- AP-42 is the emissions estimating procedures given in Supplement D, Section 4.13. It has been superseded by SIMS and Water8.
- SIMS is the Surface Impoundment Modeling System, V2.0 developed by the OAQPS and CERI for CTC. It has been superseded by Water8.
- TOXCHEM+ is a wastewater treatment plant model produced by Enviromega with support from Environment Canada and EPA.
- FATE is the Fate and Treatability Estimator Model developed by EPA's Engineering and Analysis Div. of the Office of Science and Technology. It has been superseded by WATER8.
- BASTE is the Bay Area Sewage Treatment Emissions model developed by CH2M-Hill for East Bay MUD, with help from WEF.
- Water8 is EPA's current wastewater treatment systems emission model produced by OAQPS using the procedures form SIMS, FATE, AP-42, and other EPA sources.
- CORAL and CORAL+ are models for collection system emissions estimating. Developed by Richard Corsi of U. of Texas-Austin and distributed as public domain (CORAL) and commercial software (CORAL+). It is similar to the sewer portions of SIMS but more accurate.

the area source, surface release model in TSCREEN after developing a good guess at the emission rates.

Care must be taken in using water sample based analytical results. The sampling apparatus, sample containers, and the laboratory equipment are all cleaned with or utilize acetone and methylene chloride. This can cause false positives in the analysis process for these two chemicals. EILS recommends that influent water quality samples for these chemicals be acquired separately, in containers specifically cleaned without their use, and that the laboratory understands that these two chemicals are being looked for specifically, so the standard laboratory procedures that use these chemicals do not interfere with the analysis. However, if there is reason to suspect that there is a lot of acetone or methylene chloride in the treatment plant influent and it is certain that all of the acetone and methylene chloride is removed from the sampling apparatus and sample containers prior to their use, the acetone and methylene chloride results reported from the laboratory may be trustworthy.

In order for a large wastewater treatment plant to emit more than 10 TPY of a specific TAP, there must be a single or group of related industries that are discharging relatively large quantities of the specific chemical to the treatment plant. At the levels modeled to be needed in the municipal treatment plant influent, there must be an ineffective or nonexistent pretreatment program in place. It is more likely that an industrial wastewater treatment plant will have influent concentrations that may cause air emissions to reach the 10 TPY level or have cumulative emissions that reach the 25 TPY level.

Table 2 shows the influent concentrations needed to cause an emission to exceed ten tons per year of a listed TAP.

Table 2. Wastewater Influent Concentrations in Grams/Liter at a 30 MGD Municipal Wastewater Treatment Plant to Cause an Emission of 10 TPY of the Listed TAP

TAP	Surface Aeration Influent Conc. (g/L)	Diffused Aeration Influent Conc. (g/L)
Acetone	14,996	32,135
Chloroform	287	1,103
Styrene	249	705
Toluene	1,583	4,370
Methylene Chloride	322	1,626

TAPs listed above were the most common ones reported of the volatile organic compounds analyzed by the VOA test (part of a water priority pollutant scan). These compounds are also among the list of 59 chemicals found to be most common nationwide in the wastewater influent and in the air emissions from wastewater treatment plants.

Modeling work has shown that any treatment plant expansion for a community with chlorinated drinking water needs to be looked at for compliance with ambient chloroform criteria. Aeration basin expansions of as small as 0.5 mgd with surface or diffused aeration can result in ambient concentrations of chloroform that exceed the ASIL at a reasonable fence line distance (10 meters at a small plant and 20 meters at a large facility)[†].

Currently only WATER8, TOXCHEM+ and BASTE are capable of modeling the emissions from a trickling filter. The gaseous kinetics of a trickling filter are quite similar to a stripping tower. The major difference that is obvious, is that the trickling filter has a much lower surface area and turbulence in the filter bed than occurs in a packed bed stripping tower.

The best routine sampling for determining compliance with a TAP emission limitation from a treatment plant is regular influent and effluent sampling and analysis for the chemical(s) of concern combined with use of the emission estimating model used during permitting. The influent sample collection and analysis is a relatively standard test procedure that is established in Standard Methods for the Examination of Water and Wastewater and the EPA Test Methods for water quality analysis. These tests are grab samples, analogous to a source test. The frequency of these tests should be once per month, but on a different day and time each month. If the source wants to do a series of grab samples to determine when the most typical or highest influent concentrations exist, They should take samples hourly over a 7 day period. Composite samplers capable of taking 24 hourly samples that meet the zero headspace requirements of the test procedure are now becoming available.

In order to sample the air emissions from the various treatment units at a wastewater treatment plant, is necessary to enclose the entire treatment unit and measure the off gas concentrations of the various air pollutants, or to use a flux chamber. Except for facilities that have been required to be enclosed for odor control or climate reasons, most actual source testing of the emissions from wastewater treatment processes has been through the use of flux chambers.

Various control devices may be beneficial for reducing emissions from wastewater treatment processes. VOC emissions may be reduced by means of compost beds, aerating with odorous air (2-way movement of gases from bubbles to water based on chemical equilibrium conditions), odor control scrubbers operated to maximize VOC pollution control, activated carbon following conventional odor control scrubbers and various scrubbing liquors, steel wool or iron filings for H_2S control. Other than anaerobic digester off gases, pollutant concentrations are too low and air volumes are too high to allow for

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[†] Influent Chloroform content of 6.5 ug/l

the use of flares or thermal oxidation units for emission control. Changing the method of aeration to an activated sludge process or changing the ventilation rate of a trickling filter can result in decreased emissions from those process units. Wastewater treatment plant managers and maintenance staff do not like to use activated carbon for odor (and VOC) control because of concerns about spontaneous combustion in the carbon, dangerous and hazardous waste disposal issues, on-site regeneration of the spent carbon, and loading the carbon with chemicals other than the target chemicals.

References

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 4.3 Wastewater Collection, Treatment and Storage, September 1991)
(available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Washington State Department of Ecology, *Facility/Site on the Web*, accessed 1/20/98.
(http://www.wa.gov/ecology/iss/fsweb/fshome.html)

On-Road Mobile

All mobile sources are combustion sources, and their pollution comes from small inefficient engines. Incomplete combustion is caused by lack of oxygen to the fuel source.

Method for Determining Emissions

EPA's *Procedures for Emissions Inventory Preparation, Vol. IV: Mobile Sources* should be used to determine emissions for onroad vehicles. This method is the accepted methodology therefore, there will be no discussion of alternate methods of determining vehicle emission estimation methods for this report.

Estimating emissions of toxics is a two step process. The basic steps are:

I. Vehicle Miles Traveled (VMT): determine an estimate of miles traveled in the area of concern, and
II. MOBILE5.0ah: Calculate emission factors for total organic gases using MOBILE5.0ah,
III. apply appropriate total oganic gas (TOG) speciation profiles to estimate toxic emissions.

Inventories can be made more accurate by using as specific information as possible in each of the three steps.

A general statewide inventory was performed using the three steps above and is detailed below. Inventories for state implementation plans, special studies, or other purposes would require more specific information about travel, season, control programs and other parameters.

1994 Inventory

As stated above, this inventory is based upon generalizations. Emissions were calculated for areas with and without inspection and maintenance (I/M) programs, and with and without oxygenated fuel programs. Puget Sound I/M parameters were used for all areas with I/M programs (Puget Sound, Spokane, Vancouver). A start date of 1982 was assumed for the original program and 1993 for the expansion areas. Oxygenated fuels were assumed to be used for four months in the winter. Half of the year was assumed to fall under average summer conditions, and half under average winter conditions.

Vehicle Miles Traveled

1994 Highway Performance Monitoring System (HPMS) data was used to estimate vehicle miles traveled (VMT). The WA State Dept. of Transportation (WSDOT) works with local metropolitan planning organizations to collect the traffic count data which is reported to HPMS. Detail about HPMS is beyond the scope of this report. WSDOT follows the procedures in SPECIATE.

HPMS data are collected for several different roadway classifications. Urban classifications are: Interstate, Other Freeway/Expressway, Principal Arterial, Minor Arterial, Collectors and Local. Rural classifications are: Interstate, Principal Arterial, Minor Arterial, Major Collector, Minor Collector, and Local. Volume on the Local functional system is not specifically counted, but is an assumed percentage of the other functional classifications.

The HPMS data is collected in twelve sample areas. Ten are specific urban areas. Of the other two, one is all rural, and one is all small urban. Average daily VMT (ADVMT) was 130,613,000; annual VMT was estimated by multiplying ADVMT by 365. According to MOBILE5.0ah for 1994, light duty gas cars and trucks (LDG) make up about 90% of the ADVMT and 88% of the total organic gases (TOG).

For this inventory, the Puget Sound Regional Council's 1995 roadway link file was used to dissaggregate VMT into I/M areas in the Seattle-Everett and Tacoma urban areas. Sixty nine percent of the Seattle-Everett urban area VMT and 100% of the Spokane urban area VMT were counted as under the original I/M program. The expansion area VMT was counted using 31% of the Seattle-Everett urban area and 100% of both the Tacoma and Vancouver urban areas. All other travel assumed no I/M program. Oxygenated fuels were assumed for all VMT in the urban areas of Seattle-Everett, Spokane, Tacoma, and Vancouver.

Emission Factors - MOBILE5.0a

EPA's model MOBILE5.0ah was used to generate emission factors. Inputs were as follow:

- Calendar year of Evaluation: 1994
- Month of Evaluation: July (to be more representative of 1994 VMT).
- HCFLAG: 2 (hydrocarbon components - exhaust, evaporative, running, resting)
- NMHFLG: 4 (Total Organic Gases) (also run for VOC)
- PRTFLG: 4 (all pollutants)
- RVP: 12.8, winter, 8.7 summer
- Oxygenated Fuels: 99.9% alcohol blend, 2.7% oxygen content
- Model Year Registration Distribution: 1995 Washington distribution
- Speed: an average network speed of 30 mph was used for all runs
- Average summer temperatures (Sand Point): 58 min, 72 max
- Average winter temperatures (Sea-Tac CO SIP): 34 min, 50 max
- I/M program: Puget Sound parameters, start date 1982, 1993 (expansion area)

Speciation of TOG

EPA's Speciate database profiles were used to used to speciate the M5.0a components (pollutant codes in parentheses) of TOG: profile 1305 total evaporative (V), profile 1308 running (T) and profile 1313 exhaust (X) TOG. There was no profile for the resting loss TOG. The profiles were for light duty gas vehicles (LDGV) and were given a quality rating of B. While the profile was for LDGV, it was applied to light duty gas trucks 1 and 2 (LDGT1, LDGT2) as well. Together these three vehicle types made up 88% of the TOG from mobile sources.

For oxygenated fuels runs (winter), profiles 1301, 1304, and 1314 were used respectively.

Final Emissions Inventory

The inventory applied to light-duty gasoline vehicles only. Reliable and complete speciation profiles did not exist for the other vehicle types. Emissions were calculated as tons per year. Final speciated TOG results for those toxics greater than 100 tons per year are shown in Figure 1.

Criteria Pollutant Inventory

Emissions were also calculated under the same conditions for the criteria pollutants, only for all vehicle types. The results were 1,294,171 tons CO, 177,575 tons NOx, and 146,297 tons VOC. VOC was about 94% of TOG for light-duty gasoline. It should be noted that this doesn't quite agree with the speciation profile, where VOC TOG is a lower percentage, about 87%.

Related Studies

Hydrocarbon sampling was done at several sites in the greater Puget Sound region on Tuesdays and Thursdays during the summer of 1995. Samples taken at urban areas during morning rush hour traffic (6-9am) seem to agree well with the EPA speciation profile data.

References

1990/1995 Base and Projected Year CO/O3 SIP Emission Inventories for Seattle-Tacoma, Vancouver and Spokane.

National Oceanic and Atmospheric Administration, Climatological Data, Washington, average monthly temperatures.

Puget Sound Regional Council, 1995 VMT projections by link.

Raymond, John, *Fuel and I/M Program Data*, Department of Ecology, 360-407-6856.

SPECIATE database, downloaded from the CHIEFS bulletin board 4/94.

Standard Specification for Automotive Gasoline, Annual Book of ASTM Standards.

Temperature data from meteorological station at Sand Point.

U.S. Dept. of Transportation, *Highway Performance Monitoring System Field Manual*, December 1987 and Updates, FHWA Order M 5600.1A. Office of Highway Information Management, Federal Highway Administration.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Page 13.2.1-5 (default paved road silt loading), January 1995) (available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

U.S. Environmental Protection Agency, *Draft Temperature Guidance (for 1991(2) release of Procedures for Emission Inventory Preparation, Vol. IV: Mobile Sources*, EPA-450/4-81-026d.

U.S. Environmental Protection Agency, *Final Temperature and RVP Guidance (for 1991(2) release of Procedures for Emission Inventory Preparation, Vol. IV: Mobile Sources*, EPA-450/4-81-026d.

U.S. Environmental Protection Agency, *MOBILE5.0ah, User's Guide and Model*, March 1993. Office of Mobile Sources.

U.S. Environmental Protection Agency, *PART5. Model and User's Guide*, February 1995. Office of Mobile Sources.

U.S. Environmental Protection Agency, *Procedures for Emission Inventory Preparation: Volume IV: Mobile Sources*, 1992, EPA-450/4-81-026d.

Washington State Department of Transportation, *HPMS Mileage and Daily Travel Summary*, 1994.

Figure 1. 1994 Onroad Mobile Air Toxics Emissions Estimate - Washington State

Pollutant Name	Tons	%	Cumulative Tons	Cumulative %
methane	14,883	11	14,883	11
n-butane	12,188	9	27,071	20
toluene	11,759	9	38,831	29
isopentane	8,473	6	47,304	35
ethylene	5,630	4	52,934	40
2,2,4-trimethylpentane	4,998	4	57,932	43
m-xylene	4,837	4	62,769	47
benzene	4,757	4	67,527	51
n-pentane	3,331	2	70,857	53
acetylene	3,087	2	73,944	55
2,3,4-trimethylpentane	3,054	2	76,998	58
propene	2,349	2	79,347	59
ethane	2,208	2	81,555	61
1,2,4-trimethylbenzene	2,072	2	83,627	63
methylpentenes	2,025	2	85,652	64
3-methylpentane	1,869	1	87,521	65
2-methylpentane	1,844	1	89,365	67
1-methyl-3-ethylbenzene	1,823	1	91,189	68
o-xylene	1,753	1	92,941	70
ethylbenzene	1,698	1	94,639	71
2,3-dimethylbutane	1,482	1	96,121	72
ethyl alcohol	1,410	1	97,531	73
2,3-dimethylpentane	1,313	1	98,844	74
hexane	1,307	1	100,151	75
2-methyl-2-butene	1,269	1	101,420	76
formaldehyde	1,256	1	102,675	77
s-butylbenzene	1,153	1	103,828	78
methylpropene	1,095	1	104,923	78
3-methylhexane	1,038	1	105,961	79
2,4-dimethylpentane	1,017	1	106,978	80
unc peaks to CBM non-react	976	1	107,954	81
2-methylhexane	832	1	108,786	81
2,4-dimethylhexane	791	1	109,577	82
1,3,5-trimethylbenzene	750	1	110,328	83
methylcyclopentane	747	1	111,075	83
methylpropane	740	1	111,815	84
2,2-dimethylbutane	700	1	112,515	84
trans-2-pentene	642	0	113,157	85
2,4-dimethyloctane	632	0	113,789	85
acetaldehyde	629	0	114,418	86
butene	568	0	114,986	86
2,3-dimethylhexane	561	0	115,547	86
ethyltoluene	537	0	116,084	87
1,3-butadiene	537	0	116,622	87
2,2,5-trimethylhexane	534	0	117,155	88
n-propylbenzene	509	0	117,665	88

acetone	503	0	118,168	88
o-ethyltoluene	477	0	118,645	89
1-nonene	457	0	119,101	89
1-pentene	453	0	119,554	89
2,5-dimethylhexane	446	0	120,000	90
2-methyl-1-butene	445	0	120,445	90
n-undecane	428	0	120,873	90
1,2,3-trimethylbenzene	417	0	121,290	91
butylbenzene	412	0	121,701	91
4-methyloctane	406	0	122,108	91
cis-2-pentene	377	0	122,485	92
C6 olefins	376	0	122,861	92
dimethylhexanes	372	0	123,233	92
heptane	369	0	123,603	92
styrene	360	0	123,962	93
t-2-butene	320	0	124,283	93
dimethylcyclopentane	301	0	124,584	93
methylindans	296	0	124,880	93
2,4,4-trimethyl-1-pentene	290	0	125,170	94
methyl alcohol	286	0	125,456	94
methylhexenes	275	0	125,731	94
methylcyclopentene	272	0	126,003	94
cis-2-butene	259	0	126,263	94
octane	246	0	126,509	95
unc peaks to CBM paraffins	245	0	126,754	95
c5-alkylbenzenes	233	0	126,987	95
methylcyclohexane	223	0	127,210	95
napthalene	219	0	127,429	95
1-hexene	218	0	127,646	95
n-decane	206	0	127,852	96
3-methyl-t-2-pentene	205	0	128,057	96
2,2-dimethylhexane	198	0	128,255	96
isobutylene	193	0	128,449	96
dimethylcyclohexane	193	0	128,641	96
unc peaks to CBM xylene	192	0	128,833	96
4-methylheptane	185	0	129,018	96
propane	184	0	129,201	97
trimethylcyclopentane	183	0	129,384	97
methylethylketone	181	0	129,565	97
methylbutadiene	177	0	129,741	97
cyclopentane	170	0	129,911	97
cyclohexene	163	0	130,074	97
indane	154	0	130,229	97
p-tolualdehyde	147	0	130,376	98
dimethyloctanes	140	0	130,515	98
1,2,3,4-tetramethylbenzene	138	0	130,653	98
benzaldehyde	136	0	130,789	98
ethylcyclopentane	118	0	130,908	98
3-methyloctane	106	0	131,014	98
isomers of diethylbenzene	102	0	131,115	98

Petroleum Refineries

Petroleum refineries process crude oil into many types of fuels and other useful products.

There are 22 facilities that fall under SIC code 2911 Petroleum Refining (Ecology, 1/20/98). The largest petroleum refineries in Washington are under the jurisdiction of the Northwest Air Pollution Authority (NWAPA).

Description of Process

Petroleum refineries are best represented by the Standard Industrial Classification (SIC) of 2911 *Petroleum Refining*. Other SIC codes which apply to petroleum processing include 2800 *Chemicals and Allied Products*, 4491 *Marine Cargo Handling*, and 5171 *Petroleum Bulk Stations and Terminals*.

Oil refineries are comprised of a series of complex processes which vary according to crude oil processing design, the technology which is utilized, and a number of other factors. Crude oil can be converted into thousands of products such as gasoline, kerosene, jet fuel, diesel fuel, and a myriad of other products. Refinery processes can be characterized by five major operations: (*AP-42*[1])
I. Separation
II. Petroleum conversion
III. Petroleum treating
IV. Feedstock and product handling
V. Auxiliary facilities

These operations consist of an integrated system of distillation towers, boilers, process heaters, blowdown systems, cooling towers, catalytic crackers, pumps, valves, drains, flanges, storage tanks, and a variety of other equipment and processes. Please see the Cooling Towers section for related information.

Methods of Determining Emissions

If no source-specific source tests are available, it is recommended to use emissions factors from *AP-42*.

MACT standards apply or are being developed for specific emission units at petroleum refineries. Among them are:

- Petroleum refineries NESHAP (July 31, 1995): Includes standards for petroleum refinery process units, marine tank vessels loading operations, gasoline loading rack operations, equipment leaks, and VOC emissions from petroleum refinery wastewater systems.
- Standards for catalytic cracking, catalytic reforming, and sulfur plant units (scheduled for proposal in June 1998 and promulgation in September 1999).

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[1] U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, October 1997, Document No. AP-42.

References

Keel, Lester, Northwest Air Pollution Authority, 360-428-1617. Personal communication.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 5.1 Petroleum Industry, January 1995)
(available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Washington State Department of Ecology, *Facility/Site on the Web*, accessed 1/20/98.
(http://www.wa.gov/ecology/iss/fsweb/fshome.html)

Plywood Manufacture

Plywood is an assembly of layers of wood (veneer) joined together by means of an adhesive (glue). It is a multi-use material characterized by its ability to be designed and engineered for construction and decorative purposes, flat shapes, curves, and bent shapes. There are two types of plywood: hardwood and softwood. Hardwood plywood is generally used for decorative purposes and has a face ply of wood from broad leaf trees. Softwood plywood is generally used for construction and structural purposes, and the veneers are of wood from needle bearing trees. Most plywood plants make their own veneers at plant sites.

There are approximately 42 facilities that produce plywood in Washington: 30 Softwood Veneer and Plywood (SIC 2436) and 12 Hardwood Veneer and Plywood (SIC 2435) (some of these facilities may produce both and are listed twice) (Ecology, 1/20/98).

Description of Process

A great assortment of woods are utilized in the manufacture of veneers. A high percentage of veneer produced in the northwest is manufactured from Douglas fir, with lesser quantities of veneer made from ponderosa pine and hemlock.

The various operations for converting roundwood into veneer and finally into plywood are relatively simple and chiefly mechanical.

Veneers are cut to thicknesses ranging from 1/40 to 3/8 inch. After veneers are cut, they may go directly to a clipper or they may be stored temporarily on horizontal storage decks or on reels. From there the veneers are conveyed to the dryers.

Freshly cut veneers are ordinarily unsuited for gluing because of their wetness. It is therefore necessary to remove the excess moisture rapidly, and veneers are usually dried to a moisture content of less than 10 percent. This is a level compatible with gluing, and consistent with the moisture content to which plywood products will be exposed during construction.

Several methods for drying veneers are in use. The most common type of dryer is a long chamber equipped with rollers on belts which advance the veneer longitudinally through the chamber. Fans and heating coils are located on the sides of the chamber to control temperature and humidity.

The majority of high temperature (above 100°C or 212°F) veneer dryers depend upon steam as a heat source. The heat is transferred to the air by heat exchangers. However, direct-fired oil and gas dryers are becoming increasingly common in the industry.

A number of adhesives can be used in the manufacture of plywood. For the purpose of this discussion, distinction is made between (1) protein and (2) phenol-formaldehyde and urea-formaldehyde glues, since these are the classes of glue most often used in the industry. Protein glue is extracted from plants and animals, and typical ingredients are water, dried blood, soya flour, lime, sodium silicate, caustic soda and a formaldehyde donor for thickening while the other two are synthetic, thermosetting glues. Urea-formaldehyde glues are synthetic thermosetting glues and typical ingredients are water, defoamers, extenders (wheat flour) and urea-formaldehyde resin. Phenol-formaldehyde resin are also synthetic thermosetting glues and typical ingredients include additives of caustic soda and soda ash.

Both protein and urea-formaldehyde are chiefly interior glues (less water resistance), while phenol-formaldehyde is an exterior glue (good water resistance). Urea-formaldehyde is used almost exclusively in the hard plywood industry where panels are used for furniture and indoor panelling.

Most plywood manufacturers mix their own glue in large dough-type mixers. The glue is then applied to the veneer by means of a spreader, the most common of which consists of two power driven rollers supplied with the glue. More recently the practice of applying glue by means of sprays and curtain coaters has become common.

After gluing, the layers of veneer are subject to pressure to insure proper alignment and an intimate contact between the wood layers (veneers) and the glue. The glue is allowed to partially cure under pressure. Pressing may be accomplished at room temperature (cold pressing), or at high temperature (hot pressing). Hot pressing equipment is used to cure some protein, some urea-formaldehyde, and all of the phenol-formaldehyde glues.

Most pressers are hydraulic and apply pressure from 75 to 250 psi. Cold pressers are operated at room temperatures, while hot pressers are operated at temperature up to 350°F with heat being transferred by means of steam, hot water or hot oil. Plywood pressing time ranges from two minutes to many hours depending upon the temperature of the press, size of plywood and type of glue used. Usually, the hotter the press, the shorter the pressing time.

After the pressing operation, any number of a series of finishing steps, depending upon the operation and the product desired, may be taken.

Method of Determining Emissions

A considerable amount of time was spent to locate air quality data, specifically air toxics emissions data, from plywood/veneer manufacturing. Several EPA and industry studies involving source testing were found. Most of these studies involved particleboard and waferboard plants. One study addressed a plywood plant. These studies have basically concentrated only on formaldehyde and phenol. These studies also addressed the chemical and physical nature of the emissions from the veneer dryers used in the plywood industry.

According to a Washington State University (WSU) study, the emissions from plywood veneer dryers are relatively small and almost totally hydrocarbon (mostly terpenes).

WSU estimated that a typical veneer dryer emits material (hydrocarbon) equivalent to 74 acres of a mid-latitude coniferous forested area. (WSU, 1982)

Veneer dryer emissions characteristically have a blue haze. This blue haze is due to hydrocarbon condensation after leaving the dryer stack. The particulate matter formed has a diameter in the range of tenths of microns. WSU has studied the composite of this haze in detail (WSU, 1982).

Emissions of formaldehyde and phenol from the existing plywood/veneer plants are affected by the percent free formaldehyde and phenol in the glue (resin) composition, not by how many plywood panels are being made by the plywood plants. Some major factors in determining emission rates are: 1) Age of the industry and equipment, and 2) Type of plywood being made.

If they are making high density overlays which use glues with a high percentage of free formaldehyde, the emission rate may be as high as 1.0 lbs/103 sq.ft. board. At the same time, when the industry is making low density overlays, toxics emissions could be as low as 0.025 lbs/103 sq.ft. Therefore, the recommendation to permit writers is to develop a specific emissions rate for each plywood plant, using the industry's annual glue use and glue composition. This information is provided in the material safety data sheets that the glue companies provide to the plywood industries.

References

Bamesberger, W. Lee; Malcolm Campbell and Dagmar Coran, *Size Distribution Measurements of Condensing Aerosols from Plywood Veneer Dryer Emissions*. Washington State University.

National Council of the Paper Industry for Air and Stream Improvement, *Technical Bulletin No. 503*.

Piliaris, Alex. Site visits to nine plywood/veneer plants in Washington.

Source Study by a Washington plywood plant (name confidential).

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 10.5, Plywood, September 1997)
(available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

U.S. Environmental Protection Agency, *Evaluation of Emission Factors for Formaldehyde from Certain Wood Processing Operations*, October 1987, EPA-450/3-87-023.

U.S. Environmental Protection Agency, *Evaluation of Emission Sources at a Waferboard Manufacturing Plant*, September 1987, EPA 450/3-87.

Washington State University, *Chemical Characterization of Plywood Veneer Dryer Emissions*, Final Report, April 26, 1982.

Washington State Department of Ecology, *Facility/Site on the Web*, accessed 1/20/98.
(http://www.wa.gov/ecology/iss/fsweb/fshome.html)

Polystyrene Manufacture

There are approximately 21 facilities in Washington under SIC code 3086 Plastics Foam Products (Ecology, 1/20/98).

Description of Process

Polystyrene is produced by the polymerization of styrene monomer (EPA, 1993). Styrene (CAS number 100-42-5) is a colorless liquid that evaporates easily. Expandable polystyrene is produced by introducing a volatile blowing agent which causes the polymer to expand when heated. Polystyrene is foamed through the use of physical blowing agents. Blowing agents are gases or liquids which are soluble in the molten polymer under pressure. Upon depressurization, the blowing agent volatilizes causing the polymer to foam through the formation of gas cells.

Traditionally, polystyrene foam was produced with volatile hydrocarbon blowing agents such as n-pentane, isopentane, and n-butane. Because of their highly flammable nature, they were for the most part replaced by nonflammable chloroflurocarbons (CFCs). However, concerns over the use of ozone depleting CFC-11 and CFC-12 are prompting a return to hydrocarbon blowing agents or other alternatives such as HCFC-22 (EPA, 1990).

Methods of Determining Emissions

There are three major sources of emissions: process vents, storage tanks, and equipment leaks. Secondary sources emissions include transfer and handling operations among others.

Due to the use of highly flammable VOCs each facility had been designed to remove air from the facility quickly. This high air flow hindered the ability to measure emissions accurately. The locations of the fans and vents were also difficult to access. It became clear the emissions were dependant upon the type of manufacturing process used. A literature search identified that "Insufficient information is available to develop emission factors for fugitives or process source emissions" (EPA 1993).

Two different methods could be used to develop these emission factors. One could be the amount of VOC emitted per amount of VOC purchased, the other could be the amount of VOC emitted per amount of product produced. Using available information, the confidence level in emission factors developed in this way range from low to moderate and are based on many complicating factors.

References

Agency for Toxics and Disease Registry, *Toxicological profile for styrene*, Atlanta, GA, 1992.

American Society for Testing and Materials, *Analysis of organic compound vapors collected by the activated charcoal tube absorption method - method D 3687-89,* 1989 annual book of ASTM standards, Vol. 11.03, Philadelphia, PA, 1989b, 244-248. (“”)

Bishop, RB, *Practical Polymerization for Polystyrene*, Boston, Massachusetts: Chaners Books,1971.

Boyd, BP, 1990. *Styrene: Perspectives on the Carcinogen Question*, SIRC Review. Vol 1 No. 1., Washington DC: The Styrene Information and Research Center, 9-23.

Hawley GG, et al, *Hawley's Condensed Chemical Dictionary*, Eleventh edition, New York, NY: Van Nostrand Reinhold Publishing,1987.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources,* Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 6.6.3, Polystyrene, September 1991) (available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

U.S. Environmental Protection Agency, Control *of VOC Emissions from Polystyrene Foam Manufacturing*, 1990, EPA-450/3-90-020. Office of Air Quality, Triangle Park, NC.

U.S. Environmental Protection Agency, *Locating and Estimating Air Emissions from Sources of Styrene*, 1993, EPA-454/R-93-011. Office of Air Quality, Triangle Park, NC.

Washington State Department of Ecology, *Facility/Site on the Web*, accessed 1/20/98. (http://www.wa.gov/ecology/iss/fsweb/fshome.html)

Printing

There area total of 124 commercial printing facilities in Washington, of which 83 are lithographic (SIC 2752), 2 are gravure (SIC 2754), and 39 are unclassified (SIC 2759). This report only includes sections on lithographic and screen printing.

Lithographic Printing

Description of Process

Ecology staff visited two lithographic facilities. Total hydrocarbon measurements were obtained at these facilities with a flame ionization detector during all the stages of press operation. In preparing for this report, Air Quality Program staff worked closely with Hazardous Waste Program and with Thurston County staff. Thurston county has spearheaded the hazardous material substitution specifically in lithographic facilities, and have inspected over 35 lithographers in their jurisdiction.

The category investigated includes only non-heated sheetfed, offset lithographic printers. Web-type offset presses, such as those of newspapers, were not investigated. Heated web-set presses have the potential for higher VOC emissions.

Offset lithography refers to the process of creating an image in paper from an exposed plate. The image is transferred or "offset" to a blanket cylinder after ink and fountain solution interact with the image plate. The blanket cylinder transfers the image onto sheetfed paper.

This process involves the use of inks, fountain solutions and cleaning solutions. Inks are oil based (petroleum or vegetable). Fountain solutions are water based and may contain up to 10% isopropyl alcohol plus small quantities of synthetic resins and buffers. Cleaning solutions are variable in composition including aliphatic and aromatic hydrocarbons, and less commonly chlorinated solvents such as methylene chloride.

The measurements conducted (2/2/94 and 3/8/94 reports) showed that the most significant emissions are the volatile components of blanket and roller washes and cleaners. These blanket washes may contain 20-40% toluene and/or xylene and other petroleum-derived compounds. During application, up to 1000 ppm total hydrocarbons (as methane) were measured. Measurements of the saturated vapor zone above ink and fountain solutions, were between 2 and 8 ppm (as methane). These levels remain the same during the ink roller application. During blanket and roller washing, the background press room levels rose and remained high (12-50 ppm).

Methods of Determining Emissions

The parameters that influence the press room emissions are: press operator practices, complexity of print job, order in which jobs are assigned to each press, number of presses, number of jobs per press, type of presses, and type of blanket and roller washes used.

Maximum one-hour calculated outdoor total VOC emissions (as methane) based on the highest measured values at a medium sized lithographic facility, estimated convective air exchange velocity rates, worst-case building configuration conducive to plume downwash, and the EPA model SCREEN, were 352 $\mu g/m^3$. For comparison, the acceptable source impact levels for xylene and toluene are 1500 $\mu g/m^3$ and 400 $\mu g/m^3$, respectively. Note that toluene and xylene are expected to be 20-40% of the total emissions. If the monitored facility represents the category well, this data supports the hypothesis that medium sized sheetfed offset lithographic facilities do not pose a recognized ambient air health threat. Note that this facility does not use chlorinated solvents. Certain chlorinated solvents such as methylene chloride have very low acceptable source impact levels, and thus may lead to increased ambient air carcinogenic risk.

The maximum estimated emissions from the above facility are approximately 900 pounds of VOC (as methane). A Hazardous Waste Program database is available that lists approximately 90% of the lithographic printing facilities in the state along with contact names, addresses and related information. Most of the facilities are smaller than the example used above, and it is expected their emissions would be lower.

Lithographic printer suppliers in the state were approached to obtain data on the type and total volume of products sold in the state. The suppliers were reluctant to provide such information.

The only method available to quantify the type and volume of cleaners used in the industry is to request the individual lithographic facilities to record their usage rate of blanket and roller washing products.

The press operators could be required to record the total volume of solvent and type used for each job. Aside from the benefit of collecting information, this practice could lead to reduced usage of cleaning solvents.

A second method to quantify emissions on a total VOC basis is contained in the EPA CTG document referenced below. This method utilizes an estimated rate of 0.04 gallons per unit hour based on a model plant. It is also assumed that 100% of the cleaning compound evaporates into the air. The rate is then used in the equation:
cleaning solv used = cleaning solution used rate X # units X hrs operation/yr
(gallons/year)   (gallons per unit hour)   (presses)

An industry representative (Eisenmann) believes that the EPA estimated usage rate is too high. In his facility, the estimated usage range actually ranges from 0.001 and 0.01 gallons/unit-hr.

Screen Printing

In screen printing, the ink passes through a porous screen of fine silk, Nylon, Dacron, polyester or stainless steel mesh to which a stencil has been applied. Printing is accomplished by applying ink to the screen and then forcing the ink through the stencil with a rubber or synthetic blade known as a squeegee. Inks are usually cured by applying heat, infrared (IR), or ultraviolet (UV) to the printed products. After the job is finished, the screens are cleaned of ink and stencil, then re-used.

Screen printing can print relatively heavy deposits of ink onto practically any type of surface, including fabric, plastics, metals, papers, and leather. Products printed include T-shirts, hats, printed circuit boards, signs and banners, nameplates, and containers of all kinds and shapes. The screen printing industry can generally be divided by product type into two groupings: textile printers, and flatwork printers.

Methods of Determining Emissions

VOC and HAP sources in screen printing come from the ink systems and screen cleaning solvents. A 1993 survey of Seattle area screen printer shops by King County's Metro Hazardous Waste Section's Screen Printer Project showed ink systems used as solvent based (61%), plastisol (45%), water-based (34%), and UV cured (14%).

Most of the solvent based inks are used by flatwork screen printers. These inks need to bond tightly to substrates like plastic, metal, or glass. Inks must be durable and dry quickly to avoid line spreading. Ink solvents can be xylols, toluene, ketones, and mineral spirits. Screen and tool clean up solvents are similar lacquer thinner type materials.

Textile printers use inks that are generally low in VOCs, so most emissions from these facilities will come from screen and equipment cleaning. Traditional cleaning solvents are xylene and toluene, but some printers are changing to lower VOC solvent alternatives and aqueous based products. Textile printers remove small ink contaminants from fabrics using a "blow out gun" that uses dry cleaning type solvents to dissolve and blow inking errors through the fabric on to a paper towel. Traditionally, the hottest solvent mix of 1,1,1 trichlorethylene, perchloroethylene, and methylene chloride that the printer can find is used. Mineral spirits can be used to clean some plastisol type inks.

Emissions from screen printers can only be done by a material balance based calculation. No emission factor will fit any two printers. They are all different. Major compounds to look for will be traditional ink bases and clean up solvents like toluene, xylene, MEK, other ketones, mineral spirits, and chlorinated solvents.

Material usage data combined with material composition data will be required to estimate emissions at individual screen printers. Inks and clean up solvents are the targeted materials. Production usage, purchasing records, MSD sheets, manufacturer's data sheets will be typical sources of this information.

A general method of estimation might be to estimate the usage of ten to twenty screen printers, including the largest printers. Then using a factor based on engineering judgment, apply these emission rates to the total number of screen printers registered in the state. This will probably not be accurate, but will give the best estimate possible without extensive data gathering.

One complication is that many screen printing operations are captive within another business, like a printed circuit manufacturer or airplane manufacturer. Other screen printers work out of their basement. Determination of the total number and size of screen printers in the state will be difficult.

References

Buonicore, Anthony J. and Wayne T. Davis. *Air Pollution Engineering Manual*, Air & Waste Management Association, VanNostrand Reinhold, New York, 1992, pp. 397 - 401.

California Air Resources Board, *Graphic Arts Printing Operations*, June 1992.
Eisenmann, Michael. Capitol City Press, Olympia. Personal Communication.

Kent, Michael. Thurston County. Personal Communication.

Lethe, Eric, Inland Technology Inc. Personal communication.

Noble, Jason, Sun Sportswear. Personal communication.

Metro Hazardous Waste Management, *1993 Screen Print Survey Results*, January 22, 1994.

Myhre, Brian; Rice, Darin. Ecology Hazardous Waste Program. Personal Communication.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 4.9, Graphic Arts, April 1981)
(available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

U.S. Environmental Protection Agency, *Control of Volatile Organic Compound Emissions from Offset Lithographic Printing*, September 1993. Emission Standards Division, Chemicals and Petroleum Branch.

U.S. Environmental Protection Agency, *Reducing The Use Of Reclamation Chemicals In Screen Cleaning*, EPA Design For The Environment (DfE) case study 2, EPA 744-F-93-05.

Washington State Department of Ecology, *Air Quality Program database*, 1995.
Contact: Sally Otterson, 360-407-6806.

Washington State Department of Ecology, *Facility/Site on the Web*, accessed 1/20/98.
(http://www.wa.gov/ecology/iss/fsweb/fshome.html)

Washington State Department of Ecology, *Notes on Measurements Conducted at Two Lithographic Printing Facilities*, (2/2/94 and 3/8/94). Ecology Air Quality Program Files.

Solvent Cleaning

This category encompasses a wide variety of industries engaged in cleaning a product, or a component of a product, with the aid of a surfactant, an emulsifier or a solvent other than water. There are many cleaning processes available including low pressure and high pressure sprays, power washers, immersion cleaning, wiping and vapor degreasing.

This category potentially includes over 6800 facilities, and fall into a wide range of SIC codes as shown in Table 1. This number is an estimate based on a 1992 Department of Employment Security publication.

Table 1. Number of Facilities That May Engage in Solvent Cleaning by SIC in Washington State[1]

SIC Code	Industry Classification	Number
3471	Electroplating, polishing, anodizing and coloring	46
7629	Electrical and electronic repair shops	236
3479	Coating, engraving and allied services	37
3993	Signs and advertising displays	65
3498	Fabricated pipe and pipe fittings	10
3441	Fabricated structural metal	60
7500	Automotive repair and refinishing	3382
2500	Furniture and fixtures	218
3900	Miscellaneous Manufacturing Industries	374
3600	Electronic Equipment	303
3700	Transportation Equipment	645
3800	Instruments and related products	249
3500	Industrial Machinery and Computer Equipment	856
	Estimated total number of facilities	**6855**

Table 2 contains information about the most commonly used cleaning compounds that also present adverse impacts on air quality. It is not an exhaustive list, but the compounds of greatest concern are included in the table. Other substances of little or no impact on air quality are also

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[1] Information from Employment and Payrolls in Washington State by County and Industry, 1992 Annual Averages. Washington State Employment Security Department.

used such as the higher molecular weight naphthas, soaps and detergents. The Halogenated Solvent Cleaning Maximum Achievable Control Technology (MACT) standards were predicted to reduce the emissions of chlorinated organic solvents by 63% nationwide by 1997 (FR 94-28974).

Table 2. Most Commonly Used Cleaning Compounds with Known Adverse Air Quality Impact

Compound	Reason for Concern
Methylene chloride	carcinogen
1,1,1 trichloroethane	stratospheric ozone depletion potential
Perchloroethylene	carcinogen
Trichlorofluoromethane (CFC-11)	stratospheric ozone depletion potential
CFC-113	stratospheric ozone depletion potential
Lower molecular weight hydrocarbon mixtures	reactive VOCs --participate in tropospheric ozone formation
Trichloroethylene	carcinogen
Methyl ethyl ketone and methyl isobutyl ketone	classified as Class B Toxic Air Pollutants in WAC-173-460

Due to Title 6 of the federal Clean Air Act Amendments, 1,1,1-trichloroethane, CFC-11 and CFC-113 were phased out of production on January 1, 1996. For this reason the industry is currently in an interim period of using hydrofluorocarbon compounds (HCFCs) which will be phased out in January 1, 2020. It is expected that in the long term, newer technologies such as supercritical CO2, plasma cleaning and laser ablation will replace HCFCs. SAGE (Selecting Alternatives Guide) is an EPA program available for downloading from the CTC directory on the TTNWeb Home Page (http://www.epa.gov/ttn/) that offers the user a range of alternative cleaners and processes specific to the job requirements.

Methods of Determining Emissions

Due to the variability of processes, cleaning agents and facilities described above, the only adequate method of obtaining emission estimates is through a registration process. Through the registration process, each facility would submit the following information, and perform a gross material balance: total weight (mass) of solvents purchased per year, and stored or left over from the previous year, total weight of those materials disposed of as solid or hazardous wastes or in the wastewater, the total amount of materials currently in storage. The difference would be an approximation of the amount emitted into the atmosphere per year.

It is important to note that this method of material accounting can be time consuming both for the registered source as well as for the regulatory agency. Nevertheless, it is the only way of obtaining a meaningful approximation of the types of substances and materials emitted into the air, assessing the extent of material substitution, and providing technical assistance.

References

Flick, E.W., ed., *Industrial Solvents Handbook, 4th edition*, Noyes Data Corporation, NJ 1990.

Federal Register Doc. No. 94-28974, December 2, 1994.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 4.6, Solvent Degreasing, April 1984)
(available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

U.S. Environmental Protection Agency, *National Emission Standards for Hazardous Air Pollutants: Halogenated Solvent Cleaning- Background Information Document*, EPA-453/R-93-054.

U.S. Environmental Protection Agency, *Technology Transfer Network*, TTNWeb Home Page, http://www.epa.gov/ttn/.

Washington State Employment Security Department, *Employment and Payrolls in Washington State by County and Industry, 1992 Annual Averages*.

Surface Coating

Surface coating covers a wide range of categories and emissions. In Washington, major surface coating operations include aerospace, auto refinishing, furniture finishing, metal can coating, and paper coating. Emissions depend on the type of surface coating operation and the material used for coating. Surface coating can be treated as an area source when looking at a group of sources or as a point source when looking at a specific facility.

This chapter will begin by giving an overview of surface coating as it applies to all source categories since all surface coating processes and methods for determining emissions are similar. Subsequent sections will address surface coating operations specific to Washington and give a more detailed look at these processes and their emissions.

Description of Process

Surface coating materials are primarily organic polymers dissolved in a solvent or suspended in an emulsion. The material may be applied to the product by brush or by spraying. In the process of "drying", the solvent or emulsion carrier evaporates. The organic polymer is left behind to coat the surface. Regardless of the application technique, all the volatile constituents of the finish are released to the environment. However, the application technique can determine how much finish must be used and the corresponding amount of air emissions per product.

Throughout most of history, the solvents and emulsion carriers have been volatile organic liquids. Most of the compounds comprising these solvents are toxic air pollutants under WAC 173-460. In the 1950's, the first "latex" paints were introduced to the market. Latex paints are emulsions of organic polymers with water being the primary emulsion carrier. Volatile organic solvents may still be included in the formulation to balance necessary flow and drying rates. However, their proportion is greatly reduced from "solvent-based" products. Due largely to environmental concerns, the use of water-based finishes appears to be growing rapidly in the commercial sectors.

When a finish material is rubbed or brushed onto a product, essentially all the finish material contacts the surface. For all practical purposes, this is "100% transfer efficiency". However, it is labor-intensive and does not give a reliably high-quality finish. It is only rarely used commercially. Spray coating is faster than manual application, and gives a better finish more consistently. By far the most common commercial application technique is spray coating.

In spray coating, the finish material is propelled toward the surface. The intent is that the finish material hit and stick to the surface. In practice, much of the finish material misses the surface altogether ("overspray"). The amount of overspray depends to a great degree on the shape and size of the product. Some finish material bounces off the surface, and is swept by air currents into the general spraying area. Consequently, spray coating has substantially less than 100% transfer efficiency.

Transfer efficiency differs with spray-coating technique and equipment. Table 1 summarizes characteristics of spray-coating techniques and equipment.

Table 1: Spraying Techniques used in Surface Coating

Technique	Description	Advantages	Disadvantages	Transfer Efficiency
Compressed air atomization	Conventional: 50 to 100 psi	Fine finish	Lowest transfer efficiency. Poor application in recesses and cavities.	25%-30%
	High volume, low pressure: Under 10 psi	Fine finish. High transfer efficiency.	Requires training. Poor application in recesses and cavities.	45%-55%
Air-assisted airless (sic)	Small orifice: 450 psi	Fine finish. High transfer efficiency. Moderately fast application. Good penetration into recesses and cavities. Works on a wide variety of applications.	Best with slow to medium production line speeds. Best with low viscosity materials.	40%-50%
Airless	Small orifice: 2,000 to 3,000 psi	Fastest application. Good penetration into recesses and cavities.	Coarser finish. Moderately poor transfer efficiency.	30%-35%

Method of Determining Emissions

Estimating emissions from surface coating needs to take into account the coating material characteristics and the coating technique. VOC speciation and quantity estimation can best be done by a material balance of quantity and composition of coatings used.

Surface coating emissions are covered in *AP-42*[1] in Section 4.2, which provides a table that describes how to calculate the weight of VOC emissions per volume of coating depending on what VOC composition information is available on the coating. This could be VOC by weight percent, volume percent, or in waterborne paint, as weight percent or volume percent of total volatiles, with or without water.

All coatings manufacturers are trying to develop lower VOC coatings, minimizing HAP components. Emphasis on pollution prevention practices, combined with improved control technologies should be continued.

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[1] U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, October 1997, Document No. AP-42.

References

U.S. Environmental Protection Agency, *Air Pollution Engineering Manual*, Second Edition, May 1973, Document No. AP-40.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 4.2, Surface Coating, April 1981)
(available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Aerospace Surface Coating

The majority of aerospace surface coating activities in Washington State take place under the jurisdiction of the Puget Sound Air Pollution Control Agency (PSAPCA), with lesser amounts of activity under other jurisdictions. Individual facilities submit annual toxic and criteria emissions inventories to their local air authority for review. The majority of emissions are estimated using material balances.

Auto Refinishing

There are approximately 2,230 auto refinishing facilities in Washington (*Air Toxics Emissions Estimation Methods Evaluation*, pg. 96). Table 2 shows the estimated number of facilities as found by Name Finders for the May 1996 edition of this report.

Facilities were organized by the following SIC Codes:

7532	Body Shops
7538-99	Misc. Body Repair
7549-02	Automotive Customizing
5511	New and Used Car Dealers

Table 2: Estimated Number of Auto Refinishing Facilities in Washington[2]

AGENCY	7532	7538-99	7549-02	5511	TOTAL	REGISTERED OR KNOWN SOURCES[3]
Ecology-NWRO	2	0	0	0	2	NA
Ecology-CRO	58	10	1	26	95	NA
Ecology-ERO	79	7	1	42	129	NA
BFCCAA	40	5	1	14	60	NA
NWAPA	90	10	4	41	145	88
OAPCA	103	16	1	47	167	160
PSAPCA	712	75	23	331	1,141	501
SCAPCA	119	15	4	63	201	80
SWAPCA	115	19	3	46	183	68
YCCAA	57	13	1	36	107	NA
TOTAL	**1375**	**170**	**39**	**646**	**2,230**	

Description of Process

Auto refinishing consists of four process steps which may generate air toxic emissions.

I. Surface Preparation (particulate and VOC)
II. Priming (particulate and VOC)
III. Top Coating Application (particulate and VOC)
IV. Equipment Cleaning (VOC)

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[2] Name Finders, Inc., Seattle, WA was commissioned by the Ecology Air Quality Program to provide a list of businesses with the respective SIC codes. The numbers of businesses were derived from that list.

[3] Those sources that are registered with or known by the regulating authorities.

Surface preparation is the first step in the refinishing process. The surface to be coated is prepared (sometimes sanded) so that the primer will adhere properly. Solvents are used to remove wax and other contaminants before the primer is applied.

Primers are applied to fill surface imperfections, for corrosion protection and as a bond for the topcoat. Three types of primers are in general use in the industry: precoats, primer surfacers and primer sealers.

A series of topcoats is applied over the primer. The colors (metallic or solid colors) are determined by the application of the topcoats. Topcoats are applied in either single-stage, two-stage (basecoat/clearcoat) or three-stage (mica coating) system. Three commonly used topcoats are acrylic lacquers, acrylic enamels, and polyurethanes. Lacquers comprise 34% of the refinishing coatings applied in the industry.

Lacquers are preferred because they are quick drying (via solvent evaporation). This is important for quick jobs like spot repairs. Lacquers are also easily redissolved or removed with solvents.

Acrylic enamels comprise 54% of the refinishing coatings sold and are most typically used because they provide durable, high gloss finish.

Polyurethanes are the most recent coatings on the market and provide the best durability and gloss.

Metallic color appearance in metallic paints results from the orientation of the metallic flakes (proper depth and proper alignment) which is a function of the evaporation rate of the solvent during drying. The VOC content of metallic paints is regulated at higher rates because of these critical solvent limitations.

The two-stage (basecoat/clearcoat) and three-stage applications are color or a metallic base covered by two or three coats of clear coating. The VOC content of these systems is calculated using a weighted average of base coat and clear coats applied.

Only approximately 5% of coatings applied in body shops are specialty coatings (used for unusual job performance requirements). Here again, the VOC limits are regulated at higher rates because of critical solvent limitations.

Color matching and applications techniques are critical to the quality of work done by a shop. Color matching with the original equipment manufacturer (OEM) colors is a major concern of the industry since most jobs are panel or spot repairs. Typically it is prudent for body shops to have a color mixing system in house that will allow them to mix (according to a specified formula) just enough paint for a job to avoid the expense of wasting paint and disposing of excess paint. Manufacturers bake the coatings for short times at high temperatures in large ovens before the heat sensitive accessories are installed. The technician does not have that luxury. Repair jobs are typically dried and cured at ambient temp (and humidity) or by low-bake infrared heaters.

The application techniques are a critical function of lowering VOC emissions. Current transfer efficiency (ratio of weight of solids adhering to the surface to the weight of solids applied) reported by the application equipment vendors is up to 65%.

EPA and California (*California Air Resources Board*, 1991) describe Reasonable Available Control Technology (RACT) as (it is understood that the spray painting is conducted in a spray booth of some type):

- Using low VOC surface preparation products
- Using low VOC (high-solids or water-borne) coatings
- Using gun-cleaning equipment that recirculates gun cleaning solvent
- Improving housekeeping practices
- Using/improving training programs

Method of Determining Emissions

Particulates are generated in the form of dust from the sanding process preparing the surface for coating application. Particulates may be controlled by venting them through an exhaust filter which entrains the particulate matter. Vacuum systems are available that attach directly to the sanding equipment which contains and essentially eliminates particulate emissions.

Particulate emissions are regulated under WAC 173-400. A spray booth will control the emissions of particulate (overspray) by exhausting the overspray through a filter where it is entrained. VOCs are exhausted through the filter and into the stack then into the atmosphere where they are dispersed as a function of the meteorology at the time of emission.

Article 45 of the Uniform Fire Code requires spray coating operations to have a spray booth with filters; proper air flow and ventilation and pressure measuring devices. However, several of the local air pollution control authorities (LAPCAs) reported that generally these codes are difficult for fire officials to enforce.

EPA published Low-VOC Coating Limits as part of their RACT determination for Auto Refinishers. The National Paint Coatings Association (NPCA) is in agreement with EPA's RACT Option 1. (*California Air Resources Board*, 1991)

There are low-VOC cleaners on the market (<200 grams VOC/liter vs. 730 grams VOC/liter in a typical solvent) that work well for spot repair. However, these low-VOC solvents do not serve as all-purpose solvents.

Table 3: VOC Content of Auto Refinishing Products
(1 pound/gallon = 119.829 grams/liter)

Topcoats	Pounds of VOC/Gallon of Solids	Grams of VOC/Liter of Solids
Lacquers	73	8747
Enamels	20	2397
Polyurethanes	13	1558
Basecoat	6-6.9	827
Clear Coat	5.6	671

Table 4: VOC Emissions from Auto Refinishing

Process	VOC Emissions (%)	Particulate Emissions (%)
Base Case: No controls	100	100
Surface Preparation	8	100
Mixing, Priming and Top Coat Application	72	0
Equipment Cleaning	20	0

Insufficient data is currently available to determine emissions statewide.

References

An Environmental Guide for Texas Autobody Shops, An Overview of Pollution Prevention, Rules and Permits, Small Business Technical Assistance Program of the Texas Department of Natural Resource Conservation Commission and Clean Texas, 1994.

California Air Resources Board, *Automotive Refinishing, Compliance Assistance Program,* July 1991. Compliance Division.

California Air Resources Board, *California Clean Air Guidance; Determination of Reasonably Available Control Technology and Best Available Retrofit Control Technology for Auto Refinishing Operations,* January 8, 1991. Prepared by the Criteria Pollutants Branch Stationary Source Division.

California Air Resources Board, *Summary of CA's Coating Rules by Air Pollution Control Districts and Air Quality Management Districts*, March 1994. Prepared by the Stationary Source Division Solvents Control Section.

Ron Joseph and Associates, Inc, *Transfer Efficiency Test Protocol Development and Validation in Custom Coating Facility, Final Report*, January 26, 1990. Prepared for the SCAQMD.

Sherwin Williams Technical Refinish Manual.

SCAQMD Proposed Amended Rule 1151, Motor Vehicle and Mobile Equipment non-assembly Line Coating Operations.

Staff Report, *Motor Vehicle and Mobile Equipment Coating Operations*, December 11, 1991, Proposed Rule 74.18.

Staff Report, *Motor Vehicle and Mobile Equipment Coating Operations*, June 16, 1988, Proposed Rule 1151.

Texas Autobody Shop, Standard Exemption #124, A Guide to Requirements and Record Keeping, Small Business Technical Assistance Program of the Texas Department of Natural Resource Conservation Commission and Clean Texas, 1994.

U.S. Environmental Protection Agency, *Alternative Control Techniques Document: Automobile Refinishing,* April 1994, EPA 453/R-94-031. Office of Air Quality Planning and Standards, Research Triangle Park, NC.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 4.2.2.8 Automobile and Light Duty Trucks Surface Coating Operations, August 1982)
(available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

U.S. Environmental Protection Agency, *Reduction of Volatile Organic Compound Emissions from Automobile Refinishing*, October 1988, EPA-450/3-88-009.

Schwieters, Judy. Three Site visits in conjunction with OAPCA staff.

Phone Conversations with:
EPA/OAQPS:
  Mark Morris, Author of ACT Document for Auto Refinishing
  Dave Salmon, Coauthor of ACT Document for Auto Refinishing

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  Bob Blaszczak

California:
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  SCAQMD (Abid Latif, Rule 1151 writer)
  Ventura County AQMD (Ed Cowen)
  Bay Area AQMD ()

National Paint Coatings Association (Jim Sell, President)

Washington's LAPCAs:
  BFCCAA (Pete Bosserman)
  NWAPA (Lester Keel)
  OAPCA (Jim Wilson)
  PSAPCA (Tony Agyei and Larry Vaughn)
  SCAPCA (Kelle Vigeland)
  SWAPCA (Paul Mairose)
  YCCAA (Bob Godwin)

Paint Manufacturers:
  Sherwin Williams (Mark Kruzer)

Furniture Finishing

Description of Process

Wood finishing is done on a wide variety of value-added wood products. This includes at least twelve SIC codes in millwork, cabinet making, and furniture industries. Wood finishing materials encompass a wide variety of solvent- and water-based formulations. Application techniques vary widely in material use efficiencies.

In recent years, the use of water as a solvent or emulsion carrier for wood coatings has been extended to clear varnish. "Water-based" wood finishing products represent a minority of the volume of finishes being used.

These kinds of equipment are available to apply finishes to wood products. Based on a quick survey of wood finishing businesses in OAPCA's jurisdiction, the industry is about equally split between airless, air-assisted, and HVLP equipment. As with many other elements of this sector, spray-coating technique and equipment are in a state of flux.

Table 5. Standard Industrial Categories for Coating and Finishing of Value-Added Wood Products

Industrial Category		SIC Code
Millwork (doors, trim, accessories)		2511
Kitchen cabinets		2434
Mobile homes		2451
Other prefab. buildings		2452
Other wood products except furniture		2499
Furniture		
	Not upholstered	2511
	Furniture cabinetry	2517
	Other, e.g., upholstered	2519
	Office wooden furniture	2521
	Furniture for public buildings	2531
	Shelving, lockers, fixtures	2541
	Other office furniture	2599

Wood finishing involves preparation of the wood surface by sanding and coating with some combination of “finishes”: stain, sealer, and a clear or opaque coating (i.e., varnish or paint). in the wood finishing process.

Methods of Determining Emissions

Table 6 (following page) shows the volatile organic components found in typical wood finishing products used by sources in OAPCA's jurisdiction. The "lowest found" and "highest found" columns are values indicated by material safety data sheets (MSDS) for the various finishing products.

The last column, “'normal' gallon", is an attempt at defining a “generic” wood finish. The column is the median value from the MSDS which is then weighted using a typical VOC content of about six pounds per gallon. For example, for acetone you can expect to find 0.32 pounds of acetone in a gallon of finish with a VOC content of 6.1 pounds. This represents no one wood finish, but might be used to estimate emissions from the industry as a whole.

Table 6: Volatile Organic Compound Content in Wood Finishes Based on OAPCA Source Data

Volatile Wood Finish Component	**ASIL 24 hr. average g/m^3**	**Sources reporting using material having this component**	**Lbs./Gal. Finish**		
			Lowest found	**Highest found**	**Weighted to a "normal" gallon: 6.1 lbs/gal VOCs**
Acetone	5,900	2	.53	1.36	.32
Butyl alcohol	500	7	.02	.44	.05
Butylacetate,n-	2,400	8	.09	.83	.11
Diethylene glycol monoethyl ether		1	.31	.43	.2
Dihydroxy Dinitroanthra-Quinone,1,8-,4		2	.43	.6	.2
Distillates (petroleuh)		1	.27	.27	.12
Ethanol	6,300	7	.15	.66	.12
Ethyl acetate	4,800	5	.06	.6	.08
Fthyl benzene	1,000	1	.36	.36	.17
Ethyl-3-ethoxy propionate		1	.36	.36	.17
Ethylene glycol monobutyl ether		3	.43	.76	.23
Ethylene glycol monopropyl ether		4	.31	.46	.15
Ethylhexyl-Phthalate,bis,2-		3	0	.09	.08
Formaldehyde	60	3	.01	.02	0
Hydrotreated heavy naphtha		1	1.13	1.13	.51
Isobutyl acetate	2,400	2	.68	2.13	.45

Volatile Wood Finish Component	**ASIL 24 hr. average g/m^3**	**Sources reporting using material having this component**	**Lbs./Gal. Finish**		
			Lowest found	**Highest found**	**Weighted to a "normal" gallon: 6.1 lbs/gal VOCs**
Isobutyl alcohol	510	3	.23	.93	.17
Isopropanol	3,300	15	.09	1.03	.13
Isobutyl isobutyrate		2	.17	.83	.14
Lactol spirits		8	.2	1.46	.21
Light aromatic solvent naptha		1	.43	.43	.2
Ligroine		2	.66	.66	.3
Methanol	870	7	.23	.66	.15
Methyl ethyl ketone	1,000	7	.11	.19	.15
Methyl n-amyl ketone	780	3	.22	.59	.14
Methylpentanone,4-,2-	680	12	.1	2.75	.3
Naphtha (mineral spirits)		4	.08	.15	.05
Propylacetate,n-	2,800	4	.02	.38	.04
Propylene glycol monomethyl ether acetate		3	.29	.4	.15
Toluene	400	15	.1	3.0	.33
Xylene	1500	13	.08	6.81	.69

Appendix
Alternative Methodology

Furniture Finishing Cost Analysis

This report is based on twenty-four sources in OAPCA’s jurisdiction. Of these, there are 14 cabinetmakers, 4 door/millwork manufacturers, and 6 furniture makers. They vary in size on an annual revenue basis from less than $50,000 to over $5 million. Their total TAP emissions vary from less than 100 lbs. per year to over 13 tons per year. None qualify as "major sources" under Title V of the fCAAA. Their emission rates may be weakly related to the specific business sector. There is insufficient data to determine the statistical significance of these differences. The range of variation in emissions expressed against a base of annual revenue for the three sub-sectors in woodworking were

Cabinetmakers:	.001 to .013 lbs. air toxics emissions per dollar revenue (Although one was as high as .2 lbs/$) Average about .007 lbs/$
Door/millwork:	.002 to .008 lbs. air toxics emissions per dollar revenue Average about .005 lbs/$
Furniture makers:	.005 to .07 lbs. air toxics emissions per dollar revenue Average about .04 lbs/$

In general, the larger companies had disproportionately lower emissions rates than the smaller companies. This may be an indication of better material management practices or greater advancement toward low-VOC or water-based finishes on the part of the larger businesses There is insufficient data to allow separating out industry sub-sector along with size. The following difference is statistically significant:

Wood finishing businesses having more than one million dollars annual revenue averaged about .004 lbs. air toxics emissions per dollar revenue.

Wood finishing business having less than one million dollars annual revenue averaged about .08 lbs. air toxics emissions per dollar revenue.

Data were also available on emissions from three cabinetmakers in SWAPCA's jurisdiction. Revenue data were only available on the largest of these. It is also one of the largest cabinet shops on the West Coast with about $20 million in annual revenue. Its emissions ratio of about .003 lbs/$ agrees well with the above estimates.

Data from the other two SWAPCA cabinetmakers give an indication of an emission factor in the form of lbs. air toxics per square foot of wood finished. The following details the analysis:

1. The target thickness of the dry finish is about 5 to 6 thousands of an inch (Michael Dresdner, The Woodfinishing Book, Taunton Press (1992)).
2. The average finish is about 25% non-volatile material.
3. This leads to an estimate of 65 to 80 square feet of wood coverage per gallon of finish.
4. L.J.'s Custom Cabinet Shop in SWAPCA's jurisdiction reported using 137 gallons of finish. This implies 9,000 to 11,000 square of wood coverage.
5. L.J.'s also reported 1,466 lbs. air toxics for the same period.
6. This gives an emissions factor of between 13 to 16 lbs. air toxics per 100 square feet of wood finished.
7. Lynwood Kitchens in SWAPCA's jurisdiction reported 3,611 lbs. air toxics emissions and 23,395 board feet of wood processed. Assuming single side coverage once trim and scrap are included, this gives an emissions factor of about 15 lbs. air toxics per 100 square feet of wood finished.

When dealing with an individual wood finishing operation, the best estimate of its emissions will come from a close examination of the components of the finish materials the source intends to use. This information is available from material safety data sheets. Since these are likely to change over time, the analysis should be repeated (preferably by the source) at annual reporting periods. Initially, the source can project the quantities of the finish materials it will use. In subsequent reports, the source can use purchase and inventory records. the alternative for the source is to use the factors derived above, 15 lbs. total air toxics per 100 square feet of wood finished. The quantities of individual air toxics can be taken by ratio from the "normal" gallons in Tables III or IV.

For estimating industry emissions, e.g., for rule-making, total revenue data for the wood finishing sectors of interest may be accessed from the Department of Revenue by specifying the corresponding SIC codes. The total industry air toxics emissions may then be estimated from the revenue related data, above. Individual air toxics emissions may be estimated from the "normal" gallon concentrations shown in Table 6.

Metal Can Coating

This category covers surface coating of metal of cans (SIC 3411) and metal shipping barrels, drums, kegs, and pails (SIC 3412).

Description of Process

Metal containers are made using two processes, the *two-piece can* and the *three-piece can*.

At least two can manufacturers in Washington State make two-piece aluminum beverage cans. Large rolls of aluminum sheet stock are continuously fed into a press (cupper) that forms a shallow cup. The cup is drawn and wall-ironed to form the body of the beverage can. The lid is attached after the can is filled with product, usually at another site. More recently, steel tuna fish style cans and traditionally shaped food cans have been made using the two-piece process also.

Can exteriors are often roll coated with a neutral color, like white or gray, which is then oven cured at 350-400°F. Decorative inks are then put on with a rotary printer, and a protective varnish is roll coated directly over the inks, then oven cured again.

Can interiors are spray coated with "inside spray" using airless spray nozzle. These coatings have higher VOC levels to meet tough coating requirements to protect both can contents and wall. Inside sprays are again oven cured or baked.

The three-piece can process includes traditional steel food cans, pails, and drums. These are the kind of cans that you can use a can opener on either the top or bottom. A rectangular sheet (body blank) is rolled into a cylinder and soldered, welded, or cemented at the seam. One end is attached during manufacturing. The second end is attached after the filling of the can with product.

Three-piece can emissions can come from coating the inside and outside of welded seams, from inside coatings, and from exterior base coats, inks, and over varnishes.

Method of Determining Emissions

The major source of emissions from can manufacturing is the coating process. For two-piece aluminum cans, the spraying of the interior coating and the oven curing of coatings and inks produce VOC emissions. Glycol ethers, butyl alcohol, isopropyl alcohol are among the major air toxics produced by two-piece can plants in Washington. Regulations and pollution prevention pressures are moving this industry toward aqueous based coatings with lower VOC contents. Traditional hot solvents like methyl ethyl ketone, methyl isobutyl ketone, 1,1,1-trichloroethane, and Stoddard solvent are being eliminated where possible. Three piece cans usually have an inside and outside seam coating, and sometimes have inside and outside coatings like those described for the two piece can.

Material balance is the only way to get a good estimate on emissions from can or paper coating. The parameters needed are coating usage data, coatings composition (MSDS sheets for coatings), and control equipment efficiency (if applicable),

American Can Company report that: "These facilities (three-piece cans) can use a variety of coatings on a given production day. VOC/HAP emissions are calculated from the quantity of production units and film weight of the material applied to determine the quantity of coating used. This quantity is then used to calculate actual emissions."

Emissions should be calculated individually for each facility because each facility uses a unique mix and volume of coatings.

The MACT on can coating from EPA is due out in 2000.

References

California Air Resources Board, *Metal Container, Closure, and Coil Coating Operations*. The "Process and Control" section is very understandable with illustrations and descriptions. The "Records and Data" section walks through VOC and emissions calculations.

Ecology's Hazardous Waste Program, *Washington TRI Releases and Transfers by County/Facility/Chemical*, 1992, Table A-1.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 4.2.2.2, Can Coating, April 1981)
(available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Paper Coating

This category covers surface coating of packaging paper and plastics film (SIC 2671), and other non-packaging paper (SIC 2672), plastics, foil, and paper bags (SIC 2673).

Description of Process

Paper coating is usually defined as the process of putting a complete coating across the substrate, as opposed to printing a design. The word substrate is used since paper is not the only medium coated. Plastic bags (bread, frozen food, etc.), milk cartons of paper coated with polyethylene, cellophane adhesive tape, gummed labels, and resinous impregnated paper all fall in these SIC codes. The processes are all different, yet emissions calculations have a lot of similarities. For this report, resinous impregnated paper will be used as an example.

Rolls of paper are loaded on to a spool and fed through a dip coating tray. Resins are usually phenol-formaldehyde or polyester based. The resin is metered out to the desired level on the paper, then the coated paper is oven dried and packaged in either roll or sheet form for sale. The coated paper is used for overlays on plywood and particleboard.

Emissions come from the dipping/coating process and from drying ovens. Preparation areas where resin/solvent blends are prepared can cause fugitive emissions, as can resin and solvent storage tanks. Process area fumes are usually captured by hoods and ventilation systems and treated before exhaustion. Incineration is the control technology usually used.

Method of Determining Emissions

For paper coating, emission speciation and calculation varies considerably. Each source should be individually evaluated. For the resin coating example, the solvents acetone and methanol, along with resin components like phenol, formaldehyde, and styrene will be emitted.

The pollution prevention plan obtained from Dyno Overlays in Tacoma describes their paper coating process, emissions, and emissions calculations.

References

Ecology's Hazardous Waste Program, *Washington TRI Releases and Transfers by County/Facility/Chemical*, 1992, Table A-1.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 4.2.2.6, Paper Coating, April 1981)
(available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

Transportation and Marketing of Gasoline

There are approximately 2,842 gasoline stations in Washington. Approximately 2,305 have Stage I controls, and 955 have Stage II controls. In Western Washington, there are 2,110 gasoline stations, 88% of which have Stage I controls, and 45% have Stage II controls. Based on throughput, 98% of the throughput is controlled by Stage I and 78% of the throughput is controlled by Stage II.[1]

Based upon estimate by the Washington State of Transportation, more than 2.4 billion gallons of gasoline were consumed in 1994.

Description of Process

The gasoline marketing network consists of the storage and transfer facilities that move gasoline from production to end consumption. However, this report only addresses the receipt and distribution of gasoline from retail service stations. Typically, service stations receive gasoline from 8,000 gallon tanker trucks.

Loading losses occur as organic vapors in empty tanks are displaced by the liquid being loaded into the tank.

Breathing loss is the expulsion of the vapor from the tank vapor space that has expanded or contracted because of daily changes in temperature and barometric pressure. Breathing loss emissions occur in the absence of any liquid level change in the tank.

Methods of Determining Emissions

Loading losses can be controlled somewhat by using a vapor balance system (stage I vapor controls). Stage I vapor controls are simply the retrieval of the displaced vapors in the source tank by the delivery truck. The tank truck then returns the vapors to the loading terminal.

Chapter 173-491 of the Washington Administrative Code, Emission Standards and Controls for Sources Emitting Gasoline Vapors applies to sources that store, transport and dispense gasoline. This regulation defines stage I and stage II as follows:

Stage I means gasoline vapor recovery during all gasoline marketing transfer operations except motor vehicle refueling.

Stage II means gasoline vapor recovery during motor vehicle refueling operations from stationary tanks.

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[1] This is based on an informal survey conducted in 1998. Western Washington numbers are based on the 1995 emission inventory developed for Ecology's Stage II Vapor Recovery project. Eastern Washington numbers are based on regulating authority estimates for 1997. Note that some regulating authorities only reported registered sources, therefore numbers may be slightly higher.

Ecology proposed revising these state requirements for Stage 2 gasoline vapor recovery systems, and the rule was adopted on December 24, 1997, and took effect on January 24, 1998. Stage 2 is now required at the following gas stations (Ecology, December 1997):

County	Annual Gasoline Throughout	Date Required
Cowlitz/Thurston	Over 1.2 million gallons	Currently for all existing and new stations
Kitsap	Over 840,000 gallons	By December 31, 1998
Clark, King, Pierce, Snohomish	Over 600,000 gallons	By December 31, 1998
All Counties	Over 1.5 million gallons and is sufficiently close to a residence[2]	Currently

Eastern Washington stations dispensing less than 1.5 million gallons annually will not be required to submit a notice of construction and will not be required to install stage II recovery systems. New or modified stations dispensing more than 1.5 million gallons per year will be reviewed. Stations dispensing more than 1.5 million gallons that do not have environmental or health concerns are not required to install stage II vapor recovery systems.

For uncontrolled loading operations emissions, loading loss, can be estimated by the equation below. This equation is accurate to plus or minus 30 percent.

$$LL = (12.46)(S)(P)(M)/T$$

where LL = loading loss, lb/103 gal of liquid loaded
M = molecular weight of the vapors (lb/lb-mole)
P = true vapor pressure of liquid loaded (psia)
T = temperature of bulk liquid loaded (°R = °F + 460)
S = a saturation factor

EPA has estimated that vehicle refueling emissions account for as much as two percent of the overall VOC emissions inventory in urban areas. Refueling emissions at a given Reid vapor pressure (RVP) will vary with temperature from a minimum of 1.8 grams of VOC/gallon of gasoline (winter conditions) to a maximum of approximately 9 grams of VOC/gallon of gasoline (extreme summer conditions).

MOBILE5.0a is a model that uses a regression equation to estimate hydrocarbon, carbon monoxide, and nitrogen oxides for gasoline fueled and diesel highway motor vehicles. There are

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[2] Removal of a Stage 2 gasoline vapor system is a modification of an air emission control device. To remove Stage 2 equipment, gas station managers must file a notice of construction with the local air authority and gain agency approval prior to removing Stage 2. If the gas station is near a residential area, Stage 2 may be required to control air toxics.

two basic approaches to the control of vehicle refueling emissions, generally referred to as stage II (at the pump) and on-board (on the vehicle) vapor recovery systems (VRS). MOBILE5.0a can be used to model uncontrolled levels of vehicle emissions as well as both types of VRS.

The uncontrolled refueling emission factors in MOBILE5.0a are a function of RVP, temperature of dispensed fuel, and difference in temperatures of dispensed and residual tank fuel. The result of the model is an emission factor in terms of grams of vapor emitted per gallon of fuel dispensed (g/gal). EPA recommends that states and other use MOBILE5.0a to model refueling emissions for highway vehicle emissions inventory development.

References

Standard Industrial Classification Manual. Executive Office of the United States, Office of Management and Budget, 1987, National Technical Information Services. 5285 Port Royal Road, Springfield, Virginia, 22161.

U.S. Environmental Protection Agency, *AIRS Facility Subsystem Source Classification Codes and Emission Factor Listing for Criteria Pollutants*, March 1990, EPA 450/4-90-003, Research Triangle Park, North Carolina, 27711. Office of Air Quality Planning and Standards, Technical Support Division.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 5.2 Transporting and Marketing of Petroleum Liquids, January 1995) (available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

U.S. Environmental Protection Agency, *Gasoline Marketing Industry (Stage I) Background Information for Proposed Standards, Draft November 1991*, Research Triangle Park, NC. Office of Air and Radiation, Office of Air Quality Planning and Standards.

U.S. Environmental Protection Agency, *User's Guide to MOBILE4.1*, July 1991, EPA-AA-TEB-91-01. U.S. EPA Test and Evaluation Branch, 2565 Plymouth Road, Ann Arbor, Michigan 48105.

Washington State Department of Ecology, *Focus: Managing Ozone Air Pollution through Stage 2 Gasoline Vapor Recovery Systems*, December 1997. Document No. 97-122-AQ.

Washington State Department of Ecology, Informal Survey of Gasoline Stations in Washington, January 1998. Sources: Sally Otterson, Ecology, 360-407-6806, 1995 data from Stage II Vapor Recovery Project; Myria Foisy, 509-458-2055, Lori Rodriguez, 509-575-2491, Ecology; Peter Bosserman, Benton County Clean Air Authority, 509-943-3396; Gary Pruitt, Yakima Regional Clean Air Authority, 509-574-1410; Kelly Vigeland, Spokane County Air Pollution Control Authority, 509-456-4727.

Washington State Department of Ecology, *WAC Chapter 173-491 Emission Standards and Controls for Sources Emitting Gasoline Vapors*, June 17, 1993.

Williams, Joseph, *Guidance for Gasoline Vapor Recovery in Eastern Washington*, Memorandum to Air Quality Management Team, et.al. September 30, 1994. Washington State Department of Ecology, P.O. Box 47600, Olympia, Washington 98504-7600.

Woodstoves and Fireplaces

Method of Determining Emissions

Emission factors from *AP-42*[1] are used to calculate woodstove and fireplace emissions. There will be no discussion of alternate methods of determining emission estimation methods for this report. The following information details methods, assumptions, and data sources used to develop the wood burning activity level for the various types of wood burning devices in use.

In 1990, the Bonneville Power Administration (BPA) conducted a survey of wood heating habits during the 89-90 winter season (Nelson, et al.). The BPA survey was used to develop number of households using each type of device (Central Furnace, Certified and Non-certified Inserts and Woodstoves, and Fireplaces) and how many cords they burned. Areas specifically targeted by the survey were: Puget Sound, Olympic, Spokane and Yakima.

Information gathered from various local agencies about wood species burned was used to determine the weight of a cord of wood for each of these areas. The average cord of wood weighed 2,607 pounds in the Puget Sound and Olympic areas; 3,343 pounds in Yakima; and 2,788 pounds in Spokane. This information and the amount of cords burned were used to determine activity level in tons burned for each area.

These activity levels were averaged (not weighted) for the following combinations: Puget Sound-Olympic, Spokane-Yakima. This was then used to determine the tons burned for each county scenario, as assigned below.

Scenario	Counties
Puget Sound	King, Kitsap, Pierce, Snohomish
Olympic	Clallam, Grays Harbor, Jefferson, Mason, Pacific, Wahkiakum
PS-Oly	Clark, Cowlitz, Island, Lewis, San Juan, Skagit, Thurston, Whatcom
Yak-Spk	Adams, Franklin, Grant, Klickitat, Okanogan, Skamania
Yakima	Benton, Chelan, Douglas, Kittitas, Yakima
Spokane	Asotin, Columbia, Ferry, Garfield, Lincoln, Pend Oreille, Spokane, Stevens, Walla Walla, Whitman

Other assumptions had to be made to determine emissions:

- Certified equipment was assumed to consist of 50% catalytic stoves and 50% non-catalytic stoves.
- New growth (post-1990) would occur at the same level as per 1990, i.e., the same percentage of old households (HH) using equipment would be applied to new HH.
- All woodstoves/inserts installed after 1990 is Phase II certified.
- All certified woodstoves/inserts installed before 1990 are Phase I certified.

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[1] U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, October 1997, Document No. AP-42.

Emission factors are available in *AP-42* for organic compounds, PAHs, and some metals.

For this report, the July 1993 version of *AP-42* was used. Where criteria pollutant emission factors were missing for non-catalytic stoves, factors for catalytic stoves were substituted. No substitutions were made for toxics. The results of the inventory are presented in Table 1.

References

Butler, Alan, Washington State Department of Ecology, 425-649-7103, Personal Communication.

Greef, Fred, Washington State Department of Ecology, 360-407-6099, Personal Communication.

Hansen, Hugh J., *Fuelwood Facts*, Nov. 1977, Oregon State University, p 5.

Hartman, David A., William A. Atkinson, Ben S. Bryant, and Richard O. Woodfin, *Conversion Factors for the Pacific Northwest Forest Industry*, 1976, Institute of Forest Resources, College of Forest Resources, University of Washington, p. 16.

Nabors, Ottie, Bonneville Power Administration, 503-230-4002, Personal Communication.

Nelson, Mike, Energy Extension Service, Washington State Energy Office, 206-296-5642, Personal Communication.

Nelson, Mike, and Stewart Kaufman, *Evaluating Effects of Wood Smoke Control Legislation in Washington State on Electrical Customers*, June 1990. Prepared for Bonneville Power Administration by the Washington State Energy Office and the Gilmore Research Group.

Taylor, Megan, Bonneville Power Administration, 503-230-5458, Personal Communication.

U.S. Environmental Protection Agency, *Compilation of Air Pollutant Emissions Factors Volume 1: Stationary Point and Area Sources*, Fifth Edition with Supplements, January 1995, Document No. AP-42. (Section 1.10, Residental Wood Stoves, July 1993, latest version: October 1996) (available by section on Internet at http://www.epa.gov/ttn/chief/ap42.html)

U.S. Environmental Protection Agency, *Procedures for the Preparation of Emission Inventories for Carbon Monoxide and Precursors of Ozone, Vol. 1: General Guidance for Stationary Sources,* May 1991, EPA-450/4/91-016, Table 5.8-1.

Washington Department of Ecology, *Wood Smoke Pollution Survey*, Summary Report, January 1985, p. 81. Prepared by Market Trends, Inc. and Hall & Associates.

Washington State Office of Financial Management, *1995 Population Trends for Washington State*, September 1995, Table 7.

Table 1. 1995 Woodstove/Fireplace Estimated Emissions

Pollutant Group	Toxic Name	Tons Per Year
Criteria	CO	262,143
Criteria	VOC	43,911
Criteria	PM10	35,336
Organic	Methane	6,123
Organic	Ethylene	4,077
Criteria	NOx	3,232
Organic	Benzene	1,755
Organic	Ethane	1,366
Organic	Propene	1,099
Organic	Butenes	1,055
Organic	Acetylene	980
Organic	Toluene	657
Organic	2-Methyl furan	540
Organic	Pentenes	516
Criteria	SO2	497
Aldehydes	Aldehydes	416
Organic	Furfural	411
Organic	Propane	309
Organic	Furan	292
PAH	Naphthalene	275
Organic	Methyl ethyl ketone	242
Organic	o-xylene	187
PAH	Acenaphthylene	184
PAH	Phenanthrene	142
Organic	2,5-Dimethyl furan	131
Organic	N-butane	47
Organic	i-butane	24
PAH	Fluorene	23
PAH	Pyrene	22
PAH	Benzo(a)anthracene	19
PAH	Fluoranthene	19
PAH	Anthracene	14
PAH	Chrysene	12
PAH	Acenaphthene	10
PAH	Benzo(e)pyrene	10
PAH	Benzo(b)fluoranthene	6
PAH	Benzo(g,h,i)perylene	6
PAH	Benzo(a)pyrene	5
PAH	1-Methylphenanthrene	4
PAH	Benzo(g,h,i)fluoranthene	4
PAH	Biphenyl	3
PAH	Indeno(1,2,3,cd)pyrene	3
PAH	Benzo k)fluoranthene	2
PAH	7,12-Dimethylbenz(a)anthracene	1
PAH	9-Methylanthracene	1
PAH	Dibenzo(a,h)anthracene	1

Emissions were less than 1 ton per year of: PAHs: 12-methylbenz(a)anthracene, 3-methylchlolanthrene, nitronaphthalene, perylene, phenanthrol, and phenol; Polycyclic organic matter; and Trace Metals: cadmium, chromium, manganese, and nickel.