

## **Appendix A**

### **TYPICAL SOURCES AND USES OF SELECTED CHEMICALS REGULATED UNDER WASHINGTON STATE SEDIMENT MANAGEMENT STANDARDS:**

#### **AN EVALUATION OF THE EPA RAYONIER PULP MILL EXPANDED SITE INSPECTION SEDIMENT DATA SET**

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**TYPICAL SOURCES AND USES OF SELECTED CHEMICALS REGULATED UNDER WASHINGTON STATE SEDIMENT MANAGEMENT STANDARDS:****AN EVALUATION OF THE EPA RAYONIER PULP MILL EXPANDED SITE INSPECTION SEDIMENT DATA SET****Introduction**

In 1998, EPA's contractor for the Superfund Technical Assessment and Response Team (START), E&E, conducted an expanded site inspection of the former Rayonier Pulp Mill Site, located in Port Angeles, Washington (E&E, 1998). As part of this investigation, a number of sediment samples were collected in the site vicinity and analyzed for a suite of target chemical analytes. These analytes corresponded in part to those chemicals with established standards under the Washington State Sediment Management Standards (SMS). A subset of these SMS chemicals were never detected in any of the samples, but unfortunately the analytical detection limits were sufficiently elevated such that they were above either the SQS, or the SQS and the CSL standards. Thus a direct comparison of these non-detected results to these standards was not possible. These chemical analytes are summarized in Table 1.

**Purpose**

The purpose of this paper is to evaluate the subset of chemicals listed in Table 1 as follows:

1. Identify the typical sources and/or uses of these chemicals.
2. Identify the former mill process chemicals and associated operations and ascertain if they are a plausible significant source for these chemicals.
3. Based on the above, evaluate the results and provide a recommendation as to whether these non-detected chemicals warrant further investigation (i.e. retesting at lower detection limits).

The initial operating hypothesis is that most, if not all, of the chemicals listed in Table 1 are not related to the mill process chemistry or secondary mill sources. Therefore, further investigation at lower detection limits would still result in no detections (or background detections). If uses and process chemistry support the hypothesis, further investigation at this time is not warranted.

**Typical Sources and Uses**

In order to determine typical sources and uses of the selected SMS chemicals, several key reference works were consulted. These include: ATSDR's Toxicological Profiles (ATSDR, 1997); Hawley's Condensed Chemical Dictionary, 12<sup>th</sup> Edition (Lewis, 1993); Handbook of Environmental Data on Organic Chemicals, 4<sup>th</sup> Edition (Verschuere, 2001); Merck Index, 11<sup>th</sup> Edition (Merck & Co., 1989); Handbook of Environmental Fate and Exposure Data for Organic Chemicals, Vols. I-IV (Howard, 1989); and the on-line National Library of Medicine Toxnet Hazardous Substances Data Bank (HSDB) (NLM, 2001). Based on a review of these documents, the major sources/uses of the SMS chemicals of interest were determined. These results are summarized in Table 2

**Mill Process and Operations**

The mill process chemicals and general operations have previously been summarized in Section 2.3 (Site Operations and Waste Characteristics) of the Expanded Site Investigation Report (E&E, 1998). The key process at this facility was the ammonium bisulfite procedure for sulfite-based pulp production. It used ammonia, sulfur dioxide, and water in an acidic cook of wood chips under high temperature and pressure. In addition, there was a bleaching operation. The bleach plant used (at various times) chlorine, chlorine

dioxide, sodium hypochlorite, caustic, and sulfur dioxide. Obviously, these primary process chemicals are all inorganic, and not related to the SMS compounds in Table 1. Table 3 contains a summary of the principal by products and their origin from the sulfite cook process, as presented by Rydholm (1965) in his definitive work on pulping. Other than recycle, the only compound in Table 3 of potential value is the lignosulfonates, from which vanillin may be recovered through an oxidation and separation and clean-up process. Again, none of these chemicals or compound classes is directly related to the SMS chemicals of interest. Thus, primary process chemicals or the initial process waste streams do not appear to be a source for consideration.

Secondary sources would include the combustion of the hog fuel, degradation of spilled or discharged materials, and sources associated with any large industrial operation. These are discussed briefly below.

When organic materials are burned, other organic compounds can be generated that were not present in the feedstock. They are typically referred to as PICs (products of incomplete combustion). The combustion of hog fuel has the potential to create some PICs, including selected PAHs, dibenzofurans and dioxins. However, there is no reliable technique to forecast the generation of these PIC compounds (Brunner, 1989). It is a function of feedstock, combustion time, temperature, oxygen supply, as well as other factors. In general, the SMS compounds listed in Table 1 are not primarily known as typical combustion or PIC chemicals, i.e. compounds created from uncontrolled combustion processes like the burning of hog fuel. Most would be readily degraded (burned or oxidized) under normal combustion conditions.

The wood materials (e.g. chips, hog fuel) and processed (pulped) wood far and away comprise the largest potential secondary source of material either discharged through permitted facilities or spilled. They are comprised of complex macromolecules, some of which degrade over time. There are some phenolic and benzyl alcohol base structures in wood macromolecules. Pulping may facilitate breakdown certain of these complex units to components having similar base structure over time (natural degradation). However, there is very little chemical specific information on the fate and degradation of wood or pulp in the marine (or marine sediment) environment. Specifically, of the potentially feasible degradation compounds, neither 2-methyl phenol, 2,4-dimethyl phenol, or benzyl alcohol have been reported as major degradation components (Foster Wheeler, 1998; Hon and Shiraishi, 2001). Other phenolic compounds (e.g. 3 and 4 methyl phenol) have typically been observed in sediments in the vicinity of pulp mill discharges, and may be expected. These are characteristic of natural degradation and decomposition of wood (Foster Wheeler, 1998). Under a permit agreement and associated monitoring, no chlorinated phenolics were allowed in the mill discharge since 1976. In addition, it is considered highly unlikely that pentachlorophenol was ever used in the processes at this site. If employed, it is typically at a facility that is making paper (E. Tokar, personal communication).

Other secondary operation related chemicals, such as fuels (diesel) and lubricants, solvents, hydraulic fluids, transformer oils, etc. were generally used in much lesser quantities. Releases of these chemicals, if they occurred, would typically be on a localized basis. There is no indication that the chlorinated benzenes or phthalate esters were of themselves or as major components used in any major facility operations. Also, due to their almost universal occurrence in plastics, phthalate esters are ubiquitous in low concentrations in the environment. They have been detected in remote areas and are also a common contaminant introduced in laboratory analyses; they are often detected in the "blank" runs. Thus, unless an obvious source (such as a production plant or plastics manufacturer) is identified, they are typically not pursued at low concentrations. The primary uses of the chemicals listed in Table 2 do not suggest that the plant secondary operations would be a significant contributor of these SMS chemicals. However, the phthalate esters (and possibly some phenols) would be expected in a typical municipal outfall effluent. Thus, source attribution for any detected levels of phthalates in the sediments around the mill site would also be problematic.

### **Evaluation and Recommendation**

Based upon the typical sources and uses, and the mill processes and operations, a fairly clear picture emerges. Tables 2 and 3 yield no indication that the chlorinated benzenes, phthalate esters or

miscellaneous compounds were used in significant quantity or would be detected (as a mill source) if detection limits were lowered. Background levels of the phthalate esters might be found, but not directly attributable to the mill. Nothing is to be gained by investigating these chemicals further.

The ionizable compounds warrant further discussion. The 2-methylphenol has been noted by one author as secondary source associated with pulp mills. This is undoubtedly as a degradation product of the wood or pulp, as opposed to a primary or secondary process chemical. At other pulp mill locations, Foster Wheeler has noted the other substituted methylphenols (e.g. 3- or 4- methylphenol) as present, while the 2-methylphenol remains undetected or at a lower concentration. The 2-methylphenol detection limit for the current data set is within a factor of 1.1 to 1.5 of the SMS SQS and CSL values. Given the fact that it is a degradation product (not a source chemical), other SMS phenolics are detected first, and the current detection limit is very close to the criteria, it is difficult to support an additional sampling and testing sequence to reduce detection limits.

The 2,4-dimethylphenol has not been identified as directly affiliated with sources, uses or as a degradation component. Furthermore, the SQS and CSL levels for this compound are difficult to analytically achieve, even in relatively clean matrices, and this compound is traditionally problematic for this reason. An additional sampling and testing sequence may still not achieve the desired detection limits. Thus, even a stronger case exists to conduct no further testing for this phenol

One source indicates that a secondary use for pentachlorophenol is as an additive used to control slime in the pulping process. However, there is no record of this use or application at the former Rayonier mill, and its historic use at this facility is considered highly unlikely (E. Tokar, personal communication). There are clear records that the compound had not been used for the past 25 years. Also, in the previous investigation, the detection limit was never greater than the CSL, the detection limit was greater than the SQS only 2% of the time (typically much lower), and the compound was never detected. Therefore further sampling and testing for this compound does not appear to be warranted.

Benzyl alcohol was not a target analyte in the initial round of sampling. Its major sources and uses (Table 2) do not indicate its potential presence at the site (except as a natural tree exudate). However, there is a possible potential for its presence as a degradation component of wood or pulp, based on this wood chemistry (Hon and Shiraishi, 2001). There are likely several reasons that benzyl alcohol was not an analyte in the initial rounds. It is a difficult component to analyze, and tends to break down or be lost during the preparation and analysis. The SMS SQS and CSL standards are not easily achieved, especially in a complex sediment matrix. It has a very low Koc value (hence is very mobile in soil and water – slightly soluble), and does not readily adsorb to sediments. It also tends to rapidly biodegrade in both aerobic and anaerobic conditions, and does not bioconcentrate in aquatic organisms. Thus, it would not be considered a persistent contaminant. The primary potential source has been eliminated, and given its physical properties, it is highly unlikely that the compound would be detected. Given the lack of bioconcentration, it also would not be a “driver” chemical for the site under any reasonable assessment. Thus, testing for this SMS chemical is not recommended.

In summary, no further testing to reduce detection limits is recommended for any of the selected SMS compounds as presented in Table 1. Given the current information, further investigation of these compounds is not warranted at this time.

### **References**

- Agency for Toxic Substances and Disease Registry (ASTDR), U.S. Public Health Service. 1997. *ATSDR's Toxicological Profiles on CD-ROM*. CRC Lewis Press, Inc. Ann Arbor, Michigan.
- C. R. Bruner. 1989. *Handbook of Hazardous Waste Incineration*. Tab Books, Inc. Blue Ridge Summit, Pennsylvania

Ecology and Environment (E&E). 1998. *Rayonier Pulp Mill Expanded Site Inspection TDD: 97-06-0010*. Region 10 Superfund Technical Assessment and Response Team (START). Submitted to U.S. Environmental Protection Agency, Seattle, Washington. E&E. Seattle, Washington.

Foster Wheeler Environmental. 1998. *Fate and Effect of Wood Waste in the Marine Environment*. Foster Wheeler Environmental, Bellevue, Washington.

D. N.-S. Hon and N. Shiraishi. 2001. *Wood and Cellulosic Chemistry, 2<sup>nd</sup> Edition*. Marcel Dekker. New York, New York.

P. H. Howard, Editor. 1989. *Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Volumes I – IV*. Lewis Publishers. Chelsea, Michigan.

R. J. Lewis, Sr., Editor. 1993. *Hawley's Condensed Chemical Dictionary, 12<sup>th</sup> Edition*. Van Nostrand Reinhold Company. New York, New York.

Merck & Company. 1989. *The Merck Index, 11<sup>th</sup> Edition*. Merck & Co., Inc. Rahway, New Jersey.

S. A. Rydholm. 1965. *Pulping Processes*. Interscience Publishers, John Wiley & Sons. New York, New York.

National Library of Medicine. 2001. *Toxnet Hazardous Substances Data Bank (HSDB)*. Internet site: <http://toxnet.nlm.nih.gov/> U.S. National Library of Medicine, Bethesda, Maryland.

G. A. Smook. 1992. *Handbook for Pulp and Paper Technologists, 2<sup>nd</sup> Edition*. Angus Wilde Publications, Inc. Bellingham, Washington.

E. Tokar (Rayonier). August 7<sup>th</sup>, 2001. Personal Communication. Telephone conversation with R. Kadeg (Foster Wheeler). Subject: Use of pentachlorophenol and discharge of chlorophenols at Rayonier mills.

K. Verschueren. 2001. *Handbook of Environmental Data on Organic Chemicals, 4<sup>th</sup> Edition, Volumes I and II*. John Wiley & Sons. New York, New York.

<b>Table 1: List of SMS Compounds Measured in ESI but never detected</b>		
<b>Chemical</b>	<b>DL &gt; SQS (% of stations)</b>	<b>DL &gt; CSL (% of stations)</b>
<b>SMS Additional Compounds</b>		
<b>Ionizable Organic Compounds</b>		
2-Methylphenol	100	96
2,4-Dimethyl phenol	100	96
Pentachlorophenol	2	0
Benzyl alcohol	NA	NA
<b>Chlorinated Benzenes</b>		
1,2-Dichlorobenzene	2	98
1,3-Dichlorobenzene		
1,4-Dichlorobenzene	93	58
1,2,4-Trichlorobenzene	100	100
Hexachlorobenzene	98	93
<b>Phthalate Esters</b>		
Dimethyl phthalate	4	4
Diethyl phthalate	4	0
Di-n-butyl phthalate	0	0
Butyl benzyl phthalate	67	4
Bis(2-ethylhexyl)phthalate	13	9
Di-n-octyl phthalate	44	0
<b>Miscellaneous</b>		
Hexachlorobutadiene	91	69
N-nitrosodiphenylamine	51	51

**Table 2: Summary of Selected SMS Chemical Sources/Uses**

<b>Chemical</b>	<b>Primary Sources/Uses</b>	<b>Additional Sources/Uses</b>
<b>SMS Selected Compounds</b>		
<b>Ionizable Organic Compounds</b>		
2-Methylphenol	solvent, disinfectant, chemical intermediate, resins	in auto exhaust, petroleum refining, wood pulping, photo material
2,4-Dimethyl phenol	disinfectant, fungicide, resins, chemical intermediate	in gasoline, in auto exhaust, rubber, dyes
Pentachlorophenol	wood preservative, defoliant, herbicide, fungicide, molluscicide	starch and glue preservative, slime control in pulp and paper manufacturing
Benzyl alcohol	photo developer, chemical intermediate, cosmetics	perfumes, flavoring, shellac, microscopy, in auto exhaust, tree exudates
<b>Chlorinated Benzenes</b>		
1,2-Dichlorobenzene	solvent, chemical intermediate, insecticide	lead removal, magnetic coil coolant, paints, firearm cleaner
1,3-Dichlorobenzene	fumigant, insecticide	chemical intermediate
1,4-Dichlorobenzene	insecticide, space deodorant, chemical intermediate	dyes, repellent
1,2,4-Trichlorobenzene	solvent, chemical intermediate, dielectric fluid, insecticide, dye carrier	in lubricants, in drain cleaners
Hexachlorobenzene	historic pesticide, fungicide	chemical intermediate, explosives
<b>Phthalate Esters</b>		
Dimethyl phthalate	plasticizer, insect repellent	varnishes, in rocket fuel, safety glass, phlegmatizing agent
Diethyl phthalate	plasticizer, resin solvent, wetting agent, insect repellent	cosmetics, insecticide, aspirin, in rocket fuel
Di-n-butyl phthalate	plasticizer (esp. PVCs), resin solvent, rocket fuel, insect repellent	erasable ink, paper coatings, leather varnishes
Butyl benzyl phthalate	plasticizer, chemical intermediate,	coatings
Bis(2-ethylhexyl)phthalate	plasticizer (esp. PVCs), insect repellent	formerly in pesticides, in pump fluid, erasable ink, acaricide, cosmetics, film, adhesives, paints
Di-n-octyl phthalate	Plasticizer, dye carrier	film, wire, adhesives
<b>Miscellaneous</b>		
Hexachlorobutadiene	chemical intermediate	solvent, gyroscope fluid, heat transfer liquid, in hydraulic fluid, fumigant
N-nitrosodiphenylamine	historic vulcanization retarder (esp. tires)	chemical intermediate

**Table 3. Principal By-products from the Acid Sulfite Cooking Process for Manufacturing Pulp**

<b>Compound</b>	<b>Origin</b>
methanol	methoxyl groups of the glucuronoxylan
acetic Acid	acetyl groups of the xylan
formic Acid	bisulfite oxidation of formaldehyde
formaldehyde	hydroxymethyl groups of lignan
methyl glyoxal	degradation of hexoses
furfural	dehydration of pentoses
sugarsulfonic and aldonic acids	bisulfite substitution and oxidation of sugars
sugars	hemicellulose and cellulose
cymene	bisulfate oxidation of terpenes
lignosulfonates	lignin