
Executive Summary: Treated Wood

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As part of the process outlined in Washington's *Statewide Strategy to Recover Salmon: Extinction is Not an Option* the Washington Departments of Fish and Wildlife, Ecology, and Transportation were charged to develop Aquatic Habitat Guidelines employing an integrated approach to marine, freshwater, and riparian habitat protection and restoration. Guidelines will be issued, as funding allows, in a series of manuals addressing many aspects of aquatic and riparian habitat protection and restoration.

This document is one of a series of white papers developed to provide a legitimate scientific and technical basis for developing Aquatic Habitat Guidelines. The white papers address the current understanding of impacts of development and land management activities on aquatic habitat, and potential mitigation for these impacts. Individual white papers will not necessarily result in a corresponding guidance document. Instead, guidance document development, addressing management and technical assistance needs, may incorporate information synthesized from one or more of the white papers.

The scope of work for each white paper requested a “comprehensive but not exhaustive” review of the peer-reviewed scientific literature, symposia literature, and technical (gray) literature, with an emphasis on the peer-reviewed literature. The reader of this report can therefore expect a broad review of the literature, which is current through late 2000. Several of the white papers also contain similar elements including the following sections: overview of the guidelines project, overview of the subject white paper, assessment of the state of knowledge, summary of existing guidance, recommendations for future guidance documents, glossary of technical terms, and bibliography.

Focus of the Assessment

This white paper provides an assessment of current research on chemical contaminants in treated wood and the potential for adverse impact to salmon listed under the Endangered Species Act as well as other aquatic resources. The assessment focuses on recent (within the past 10 years) field-oriented studies that evaluate the spatial and temporal distribution of toxic constituents used in treated wood. However, most of the field studies specifically addressing treated wood installations did not address salmonids as a targeted receptor.

Types of Wood Structures Studied

Evaluations of treated wood structures were generally restricted to smaller installations such as bridges, docks, dolphins, or bulkheads. No studies of large installations were found. Larger installations of treated wood (e.g., greater than 50 pilings) are generally associated with waterfront property in industrial areas and municipalities. The assessment of potential impacts associated with the use of treated wood in larger installations is likely confounded with other sources of anthropogenic contamination and environmental stress. For both large and small installations, any attempt to assess potential impacts of the use of treated wood should include an assessment of cumulative impacts. Hypothetical examples are provided of The Council of Environmental Quality's four types of cumulative effects, which are based on the number of actions and how they interact.

Major Types of Wood Treatment

The potential impacts resulting from preservatives found in three major types of treated wood are addressed: creosote, ACZA (ammoniacal copper zinc arsenate), and CCA Type C (chromated copper arsenate). Creosote used as a wood preservative is a distillate of coal tar produced by high temperature carbonization of bituminous coal. The contaminant of interest in creosote-treated wood is a complex mixture of polycyclic aromatic hydrocarbons (PAH). Polycyclic aromatic hydrocarbons have metabolic intermediates that are carcinogenic and, under chronic exposure, may induce developmental toxicity. Contaminants associated with ACZA and CCA treated wood include copper, arsenate, zinc and chromate, of which copper provides the greatest risk to aquatic organisms. Effects were addressed for freshwater, estuarine, and marine environments.

Water Quality and Sediment Standards

Contaminants that migrate from treated wood by either diffusion or leaching can be compared to water or sediment quality standards and benchmarks. It is concluded that water quality standards for metals are generally appropriate for the protection of aquatic organisms; however, existing standards for sediment and for complex mixtures of PAH need to be re-evaluated in terms of potential for impacts to biota and sediment accumulation. Recent research associated with oil spills has provided more toxicological information on low-level chronic exposure to PAH that may be useful for assessing sediment and water quality standards or benchmarks. (The studies of Heintz et al. (1999) and Carls et al. (1999) provide a foundation for establishing an ecological toxic benchmark of 0.4 to 1.0 µg/L total dissolved PAH based on developmental toxicity in cold water fish. Similarly, concentrations of total PAH dissolved in water from creosote treated wood could be expected to exert the same influence on aquatic life as that demonstrated with weathered oil.)

Overall Conclusions

The overall conclusions of this assessment include the following:

- The propensity for trace metals (from wood treated with ACZA or CCA Type C) or PAH (from wood treated with creosote) to result in long-term water column impacts are much lower than their potential for impacts to sediment. Short-term acute toxic impacts are possible, but the decrease in diffusion or leaching rates of contaminants over time reduces the risk of acute impacts in the water column.
- For the size of treated wood structures evaluated in this review, the spatial extent of impact is generally small and limited to areas in the immediate vicinity of the structure. Extra consideration needs to be given to large treated wood projects.
- The relative hazard of creosote treated wood is generally greater than the hazard associated with CCA Type C or ACZA treated wood in terms of temporal and spatial impact. Consideration needs to be given to site-specific conditions.

CCA Type C or ACZA treated wood is generally preferred to the use of creosote treated wood as a more environmentally friendly product.

Creosote Treated Wood

Adverse environmental effects associated with creosote treated wood are manifested in the accumulation of contaminants in sediment and direct impacts to biota that may colonize the treated wood structure. Critical impacts resulting from the installation of creosote treated wood are dependent on the amount of treated wood installed, and the physical condition of the installation site. Creosote treated wood is not allowed in lakes in Washington and has increasingly limited use in rivers in inland Washington. In Puget Sound and along the coast historic use in estuarine and marine environments is rapidly declining due to ESA considerations for listed salmonids.

It is the chronic release of PAH that ultimately impacts the sediment and associated benthic environment. Key physical variables are the turn over of water (currents or tidal action) and the sediment characteristics. The key sediment characteristic for PAH is organic carbon content. These variables will have great impact on the fate of contaminants in the sediments. Under oxidizing conditions, PAHs can be metabolized by microbes and degraded. Implementation of BMP processing has likely reduced the amount of excess creosote on modern treated wood products compared to earlier processes.

The duration of diffusion of PAH from the retention zone of creosote treated wood is a long-term process that may last the life of the product. Pilings over 50 years old still contain sufficient amounts of creosote to kill herring embryos (Vines, et. al., 2000). The spatial impact of creosote treated wood, based on increases in sediment PAH, was localized (less than 10 meters [33 feet] for the small structures studied. No studies were found that evaluated the spatial extent of PAH attributed to large creosote wood structures (e.g., > 50 pilings).

Metals-Based Treated Wood

Long-term adverse environmental effects associated with CCA Type C and ACZA treated wood are manifested in the accumulation of contaminants in sediment and direct impacts to biota that may colonize a treated wood structure. Leaching rates of trace metals (primarily copper) from installations of CCA Type C and ACZA treated wood are greatest when the wood is first immersed in water. Comparatively, ACZA has initially higher rates of copper leaching when compared to CCA treated wood, however, leaching rates diminished more quickly in ACZA treated wood than in CCA treated wood. The differences between CCA Type C and ACZA treated wood are minor. More important, however, is that most environmental evaluations of metals based treated wood was conducted on CCA treated southern yellow pine. Additionally, most of that research was conducted in marine or estuarine environments.

The impact to the water column is a short-term event (days to weeks) and contaminants that are leached are ultimately deposited into sediments. Metals will not in the long term degrade; however, they may become mineralized, chemically sequestered, or physically sequestered. The role of acid volatile sulfides in bioavailability of metals is unresolved at this point, but likely is a major factor.

Impacts of leached metals to sediments were localized at and immediately adjacent to small treated wood structures. Increases in sediment metal concentrations were limited to within 10 ft or less of small treated wood structures in marine and freshwater habitats.

No adverse biological impacts from either sediment toxicity testing or *in situ* community changes were reported in the field studies reviewed. Adverse biological impacts were documented in Florida studies in areas of low water exchange where contaminants had accumulated in the sediments.

Impacts to Salmon

The most probable route of exposure to leached or diffused contaminants from treated wood for salmon is through the consumption of contaminated prey. Hence, exposure is greatest for salmon when they are feeding in areas of sediment deposition (low flow areas) immediately adjacent to treated wood structures. Once juvenile salmon enter larger rivers or engage in an open-water marine life stage, the potential to be adversely impacted by treated wood contaminants is very low. Areas where there are a large number of creosote treated structures pose the greatest risk to listed salmon. It is uncertain if that risk is significant (the actual intake

of PAH from treated wood has not been quantified) and that the resulting exposure in those situations results in appreciable harm to migrating salmon. However, for ESA listed species the precautionary principle should be applied to reduce risk. For potential mitigation strategies for impacts to salmon, see the mitigation section below.

Data Gaps

Specific data gaps and research needs pertaining to this assessment of treated wood include the following:

- The influence of pH should be incorporated into the derivation of water quality standards for some metals, in particular, copper.
- Sediment quality standards for metals and organics need to be normalized to those variables that control their biological availability and potential toxicity (TOC, AVS, percentage fines, etc.).
- The relationship between hepatic lesions and reproductive biology of flat fish and sediment contaminants needs to be quantitatively evaluated to assess the combined and individual dose responses of PAH, chlorinated pesticides, PCBs, and trace metals. Early life stage exposure also needs to be evaluated when assessing impacts and developing sediment benchmarks.
- A better understanding is needed of elevated tissue burdens of contaminants in biota and any adverse effect that can be associated with that burden.
- Models for predicting effects of treated wood need to be evaluated in more detail.
- Avoidance behavior of aquatic organisms to chemical contaminants released from treated wood needs further evaluation.
- Metabolic transformation and photo-oxidation need to be better understood to evaluate the risk of PAH in aquatic habitats.
- Microbial and physical degradation processes for PAH need to be better understood to evaluate long-term risk of PAH in sediment.
- A better understanding is needed of diffusion rates of PAH from creosote treated pilings prepared under best management practices.

Potential Mitigation Strategies

While this white paper focuses primarily on impacts to salmonids, the preservation of wild salmonid populations is dependent on the preservation of suitable habitat and the biodiversity associated with healthy ecosystems. Therefore, suggested mitigation strategies include general strategies as well as those that are designed specifically to reduce impacts on salmon.

General Mitigation Strategies

For new installations, other materials could be used, such as metal, concrete, or other composite materials. Work may be scheduled to avoid exposure to contaminants. In addition, treated wood may be treated further to minimize release of chemical contaminants to the environment. Mitigation for the effects of existing structures could include placing sleeves over pilings to prevent spawning on pilings, installing additional spawning surfaces, and removing the installation. Where sediment is contaminated, pilings could be cut off below sediment grade and capped with clean sediment, leaving the butt intact but isolated from the surface sediments.

Salmon-Specific Mitigation Strategies

To reduce impacts on spawning salmon, creosote treated wood should not be installed in spawning areas of listed species of salmon. If metals based treated wood is to be used in areas where salmon spawn, then installations should be scheduled to allow for sufficient weathering to occur to avoid exposure to eggs and larvae and minimize exposure to juvenile salmonids. The amount of metals based treated wood that is immersed in water should be minimized where possible if it is used.

To reduce impacts on juvenile salmon, creosote treated wood structures should not be constructed in low flow areas (i.e., small tributaries) where juvenile salmon are migrating, or where they may feed for extended periods of time (nursery areas, estuaries). Metals based treated wood structures can be used in these situations, but again mitigation should be considered to minimize exposure to sensitive life stages of listed fish and consideration given to cumulative impacts.

Treated wood should be inspected before installation to ensure that there are not any superficial deposits of preservative material on the wood. To minimize releases of contaminants to the environment treated wood stored at construction sites before installation should be managed.

As policies for the installation and operation of treated wood structures in aquatic habitats are established, professionals working in the fields of aquatic toxicology, aquatic risk assessment, and resource management should be included in the process.

WHITE PAPER

**Treated Wood Issues Associated with
Overwater Structures in Marine and
Freshwater Environments**

Submitted to

Washington Department of Fish and Wildlife
Washington Department of Ecology
Washington Department of Transportation

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Note:

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Overview of Aquatic Habitat Guidelines Project

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This document is one of a series of white papers developed to provide a scientific and technical basis for developing Aquatic Habitat Guidelines. The white papers address the current understanding of impacts of development and land management activities on aquatic habitat, and potential mitigation for these impacts. The following topics are addressed in the white paper series:

- Over-water structures - marine
- Over-water structures - freshwater
- Over-water structures - treated wood issues
- Water crossings
- Channel design
- Marine and estuarine shoreline modification issues
- Ecological issues in floodplain and riparian corridors
- Dredging - marine
- Dredging and gravel removal - freshwater

Individual white papers will not necessarily result in a corresponding guidance document. Instead, guidance documents, addressing management and technical assistance, may incorporate information from one or more of the white papers. Opportunities to participate in guidelines development through scoping, workshops, and reviewing draft guidance materials will be available to all interested parties.

Principal investigators were selected for specific white paper topics based on their acknowledged expertise. The scope of work for their projects requested a "comprehensive but not exhaustive" review of the peer-reviewed literature, symposia literature, and technical (gray) literature, with an emphasis on the peer-reviewed literature. Readers of this report can therefore expect a broad review of the literature, which is current through late 2000. The coverage will vary among papers depending on research conducted on the subject and reported in the scientific and technical literature. Analysis of project specific monitoring, mitigation studies, and similar efforts are beyond the scope of this program.

Each white paper includes some or all of these elements: overview of the Aquatic Habitat Guidelines program, overview of the subject white paper, assessment of the state of the knowledge, summary of existing guidance, recommendations for future guidelines, glossary of technical terms, and bibliography.

The overarching goal of the Aquatic Habitat Guidelines program is to protect and promote fully functioning fish and wildlife habitat through comprehensive and effective management of activities affecting Washington's aquatic and riparian ecosystems. These aquatic and riparian habitats include, but are not limited to rearing, spawning, refuge, feeding, and migration habitat elements for fish and wildlife.

Introduction

This white paper is an assessment of chemical contaminants in treated wood and the potential for adverse impact to salmon listed under the Endangered Species Act (ESA) and other aquatic resources when used in “over water” and “in water” structures (collectively captured as over water structures).

Treated wood is used in many outdoor applications because of its resistance to biological decay. Resistance is accomplished by adding chemicals to the wood to stop bacterial, fungal and others forms of biological attack. This assessment focuses primarily on two types of treatment: 1) organic (oil base) treatment with creosote, and 2) inorganic (water base) treatment, specifically ammoniacal copper zinc arsenate (ACZA) and chromated copper arsenate (CCA Type C). These three types of treated wood dominate the applications of treated wood in and around aquatic environments in Washington. Creosote and pentachlorophenol treated wood are not allowed in freshwater lakes (WDOE/WDFW 1995). Pentachlorophenol is not used as a supplement to creosote treated wood destined for marine applications in the northwest. A great deal of study has been performed on the toxic constituents used to treat wood, some in direct association with the use of treated wood products, but most comes from studies of the environmental fate and effects of polycyclic aromatic hydrocarbons (PAH) and trace metals [copper (Cu), zinc (Zn), chromium (Cr), arsenic (As)] and their association with other anthropogenic activities (e.g., urban run-off, mining, industry etc.). Over the past ten years, there have been a number of field-oriented studies that have evaluated the spatial and temporal distribution of toxic constituents used in treated wood. These more recent studies allow for a more direct assessment of the potential adverse impacts and ecological risk associated with the use of treated wood in and around aquatic habitats.

Background

Installation of treated wood into aquatic habitats

Use of treated wood for over- and in-water structures can result in the release of wood preservatives into aquatic habitats by three mechanisms:

1. Over-water structures can release preservatives in rain or snow melt that then runs into a body of water where they are viewed as contaminants. Activities on the structure may also dislodge treated wood fibers that in turn may fall into a body of water and form a source of contaminant entry. In-water structures can release preservatives directly into the water column. There are three exposure vectors to consider here:
 - Aquatic organisms can be exposed to released contaminants in the water column
 - Released contaminants can settle onto the adjacent sediments
 - Aquatic organisms that attached themselves (or their eggs) to immersed treated wood can be directly exposed to the preservatives in treated wood
2. Treated wood emplaced in sediments can release preservatives directly into the sediments. Subsequent removal of these structures can disperse contaminants into the water column.

This assessment will focus on direct exposure to these toxic constituents by target organisms (i.e., salmonids listed under the Endangered Species Act) and indirect exposure primarily by food chain transfer. Habitat degradation, due to impacts to other forms of biota, will be addressed. In this context, it is important to recognize that when the focus of an assessment is the evaluation of impacts on a population of organisms, the risk of those impacts can be addressed at the population level. When dealing with populations of listed species, the assessment assumes a higher margin of safety as the value of individual organisms to that population increases. The requirement to address “take,” as defined in Section 7 of the Endangered Species Act, provides a basis for this shift in emphasis, however, it logically follows that the smaller the population of a listed species, the more critical and significant individuals in that population become. To illustrate this point, consider the situation with Snake River sockeye salmon. Runs of sockeye salmon into the Snake River Basin have been less than 1,000 fish since 1970 and less than 100 since 1981 (Chapman et al. 1991). Counts past Ice Harbor Dam have shown an average escapement of 20 fish from 1985 to 1988 with two fish returning in 1989 and none in 1990. In 1991, however, eight fish passed Lower Granite Dam and four have been

observed at Redfish Lake. In 1992 one male was collected. In 1993 and 1994, 12 and 2 fish returned, respectively. By default, ESA is managing to the individual fish for sockeye. Additional rationale for this approach was discussed by the U. S. EPA (1997) and U. S. Fish and Wildlife (1993). This distinction may require additional conservatism (precautionary principle) in the evaluation of risk and subsequent recommendations arising from assessments where uncertainties about exposure and probable effects exist.

Types of Treated Wood

This section will discuss three major types of treated wood used in Washington State around freshwater and marine habitats. These are Creosote, AZCA (Ammoniacal Copper Zinc Arsenate) and CCA Type C (Chromated Copper Arsenate). Creosote and ACZA are common on the west coast and CCA Type C is used on over-water structures in Washington. Treated wood is manufactured under specific procedures design to assure maximum fixation, minimizing potential environmental impact, and waste minimization processes (WWPI/CITW 1995, AWWA 1996). Additional information on creosote, AZCA, and CCA Type C treated wood is provided in sections II and III of this report.

Drivers

The primary driver of this initiative is the potential for toxic constituents used in treated wood to affect salmonids listed under the Endangered Species Act (1973; see 50 CFR 170). Affects may be direct, and in the context of this assessment, involve direct exposure to diffusible constituents in treated wood and to contact with the wood. Diffusible constituents include chemicals that migrate from treated wood in either a truly soluble form or as a diffusible agent (micro-droplet or particulate) and are present in the water column or incorporated into the sediments. While focusing on treated wood specifically, it is acknowledged that other aspects of treated wood installation (used of plated hardware, drilling) can also introduce contaminants into the aquatic environment. To complement direct exposure, indirect exposure arises when contaminants become incorporated in the food web and are ingested by other organisms.

Existing Regulations and Guidelines

Water and sediment quality guidelines have been established for PAH and trace metals at both the Federal and State level. There are no State or Federal regulations that establish contaminant levels as a result of the use of treated wood. There are, however, memoranda of understanding, guidance, and permitting processes established by government agencies to manage the use of treated wood. Treated wood projects that have the potential to impact salmonids listed under the Endangered Species Act require review by the National Marine Fisheries Service. Other listed animals require review by the U. S. Fish and Wildlife Service.

Standards

Adopted water and sediment standards have been in effect for several years and generally reflect assessments and evaluations that predate their date of issue on the order of years. Advances in aquatic toxicology and environmental assessment have made many advances in the ensuing period of time. While a lot remains unknown about assessing exposure and effects in the aquatic environment (marine and freshwater), a lot of research has better defined the toxicity of contaminants associated with treated wood. Applicable research on the sub-lethal effects of trace metals and PAH were reviewed where they may better define the hazard and risk of these materials in aquatic environments. State standards are discussed in more detail in subsequent sections of the white paper.

Water Quality Standards

State water quality standards are contained in WAC-173-201A Water Quality Standards for the Surface Waters of the State of Washington and are discussed in this report as points of reference. Washington State water quality standards were last updated in 1997 and cover metals. There are no State criteria for PAH, either as individual compounds, fractions (low and high molecular weight compounds), or total PAH.

Marine sediment quality standards were last updated in 1995 (WAC 173-204-320). Freshwater and low salinity sediments are addressed on a case-by-case basis. Standards are listed for PAH and metals. There has been a great deal of research in the area of sediment criteria and toxicity in marine and freshwater systems. Current sediment criteria are in need of review and revision.

Memoranda of Understanding

In 1995, the Washington State Departments of Ecology and Fish and Wildlife entered into a Memorandum of Agreement for the use of treated wood in aquatic areas. Key requirements of this agreement dictate that treated wood products prepared under best management practices be used in the state. There is a provision for the recycling of salvaged treated wood that may have been manufactured prior to the implementation of BMPs. The conditions set forth in the agreement apply to both over-water, as well as in-water uses of treated wood, however, there is a recognition that over water applications may not be held to the same conditions applied to in-water applications, but BMP treated wood must be used. Where applicable, installation practices that minimize chemical and material releases into the aquatic environment will be used. When structures constructed with treated wood are no longer used, timely removal or maintenance should occur with minimal impact to the environment. Additionally, the agreement specifies that creosote and pentachlorophenol treated wood will not be used in freshwater lakes.

Position Documents

The National Marine Fisheries Service has issued a “position document” (NMFS 1998) addressing the use of ACZA, CCA, and creosote treated wood in the lower Columbia River (McNary Dam to the mouth) that is administered out of their Portland Office. The guidance

focuses on juvenile life history of salmonids and exposure concentrations based on theoretical piling structures, a regimen of river flow rates, and creosote, CCA, and ACZA treated wood

While non-binding, the Canadian government has also issued guidelines for the use of treated wood in Canadian waters (Hutton and Samis 2000). These guidelines mirror much of the guidance detailed by the Washington State MOU (DE/WDFW 1995) and require a review and permitting prior to the installation of treated wood. Treated wood installed in aquatic habitats requires the use of BMP treatment and environmental reviews to approve the projects. In other respects, they are less restrictive than practices in Washington State in that they allow the use of pentachlorophenol and creosote for specific situations in freshwater.

Cumulative Impacts

Cumulative impacts were originally defined by the Council of Environmental Quality (CEQ) to simply address the interaction of impacts associated with one activity on another activity. For example, toxicity associated with a treated wood structure may be exacerbated by effluents from an industrial outfall. The intent of the CEQ was to assure that an impact of low or questionable significance needed to be evaluated if the impact was exacerbated by other activities. Though simplistic in its original narrative form, the application of this principle expands in terms of time and space and is very difficult to quantify cumulative impacts as the number of contributing activities or impacts increases, particularly where assigning what percentage of an impact can be attributed to one activity or the other.

The Council of Environmental Quality (CEQ 1997) has identified four types of cumulative effects based on number of actions and how they interact. These four types can be illustrated with a hypothetical example of a treated wood installation of a dock with hypothetical effects. These 4 types of cumulative effects demonstrate increasing complexity of impacts and the hypothetical example was created to illustrate the complexities of this concept.

Type 1

Single effect -Repeated additive effects – a sequence of events with incremental impact - for our example, a creosote dock installation is used by juvenile fish for shelter. The juvenile fish feed on epibenthic fauna that live on the dock and adjacent sediments. This food supply contains PAH that, when metabolized, form toxic metabolites. Sub-lethal effects also include reduced vigor, slight narcosis, and reduced growth. This effect occurs year after year for each year-class that resides near the dock and feeds on epibenthic fauna growing on the dock. Taken by itself, it represents a simple additive effect. The longer the fish feed there, the greater the effect, and it repeats year after year.

Type 2

Interactions between stressors and receptors that are non-linear (sum is greater than the parts). The dock in our example is also a haven for predatory fish (bass) that feed on the juveniles. The population of juvenile fish is not only physiologically impacted by PAH exposure, but due to loss of vitality, they are more susceptible to predation by the resident predators. Hence, there are two impacts to the juvenile population that are interwoven and related. The two effects result in a greater impact to the population than what would be expected from each effect acting independently.

Type 3

Multiple actions – additive effects (this is the classical type of cumulative effect originally and simplistically defined by the CEQ). In our hypothetical example, the dock is also situated near a storm water return that introduces contaminated storm water run-off containing PAH from car exhaust into the area. The combine exposure of PAH from the dock and urban run-off are additive. Together, they result in higher levels of PAH in the juvenile fish.

Type 4

Interactive effects from multiple stressors. As a follow on to Type 3, the urban run-off is much warmer than the lake water and the warm water introduces a thermal stress that makes the fish more susceptible to exposure to PAH. In this case, the rate of transformation of PAH may go up because of the warmer water, the juvenile fish become more stressed and could even become more susceptible to disease. The predators, which are more suited to warm water, need to consume more prey and eat more of the juveniles near the dock. So for Type 4, you have multiple stressors operating with multiple effects that are interactive.

While the aforementioned example is hypothetical, it was constructed on real situations and interactions put together to demonstrate increasing complexity. Quantifying impacts of increasing complexity is difficult and carries a high degree of uncertainty, particularly when assessed against high natural variation and seasonal or annual fluctuations in habitat characteristics. In these situations where exposure to contaminants and estimates of risk are inherently uncertain, it is both realistic and desirable to invoke additional conservatism in the assessment process (i.e., precautionary principle). Recent improvements in understanding the mechanisms of toxicity and ecologically relevant endpoints, as well as environmental fate and exposure of contaminants, have worked to reduce some of the uncertainty associated with these assessments for treated wood. Nonetheless, there is still considerable debate regarding the use of treated wood and its potential impact to aquatic ecosystems.

The concept of precautionary principle should be viewed as an overarching principle to guide decision making in the absence of empirical or predictive (risk assessment) certainty (Santillo et al. 1998). As such, its basis is grounded in science and should be a driver for needs to resolve questions where uncertainty is high. Given the rather simplistic examples of cumulative effects

above and the potential for uncertainty in complex habitats with multiple human stressors, the application of precautionary principle is mandated.

Salmon Life History and Exposure

To understand both direct and indirect exposure pathways, basic aspects of the life cycle of salmonids must be understood. Salmon are anadromous species that spawn in freshwater. Adults migrate from marine environments into freshwater streams and rivers to spawn. Eggs are deposited into nests called “redds” and are fertilized and covered with gravel by the adults. Spawning usually occurs in streams and rivers during the fall and winter. Some species spawn in habitats with a greater percentage of fines in the substrate, but all spawning habitats require a sustained interstitial flow of well-oxygenated water. After hatching, juvenile salmon migrate to the ocean where they reside until reaching adult status and then return to freshwater to breed.

Once the eggs hatch, migration of the juvenile fish can take two paths involving short and extended residence in fresh water. The young, as is the case with fall Chinook salmon that spawn in the main stem of the Columbia River, begin their migration to the ocean after they hatch and will spend minimal time in freshwater (Healey 1991). In contrast, spring Chinook offspring typically reside in freshwater for a year before migrating to sea. The presence of dams lengthens their occupation of main stem river habitat, however, Chinook salmon that hatch in March may enter the Columbia River estuary by June. As these juvenile fish enter estuaries and the ocean, they will be more prone to inhabit sheltered areas and near-shore areas where they will feed until they reach an appropriate size where they can compete and feed in open water. While in freshwater, their diets are composed of invertebrates dominated by insect larvae and crustaceans. In estuarine environments, marine invertebrates such as amphipods, shrimp larvae, and small fish dominate the diet (Healey 1991). There is some indication that juvenile Chinook salmon may consume small, segmented worms (oligocheates) that are common to organically enriched sediments found in industrialized areas. Pink and chum salmon also tend to stay in estuarine areas when first entering marine areas. Last, juvenile salmon may inadvertently ingest sediment that can act as an additional exposure pathway to sediment bound contaminants (Heard 1991). Tar balls have been observed in the stomachs of juvenile salmon collected in the Duwamish River^a.

The juveniles of other species and races of salmon (e.g., spring Chinook, coho, sockeye) and steelhead differ from this general pattern by their residence time in freshwater. In this case, the newly hatched juveniles spend up to a year in freshwater before migrating to the ocean and entering the marine environment. Snake river sockeye may spend as much as two years in freshwater before migrating out to sea. When entering the marine environment, the larger smolts assumed a pelagic (open water) life style more quickly and move into open water sooner than fall Chinook salmon.

^a T. Collier, National Marine Fisheries Service, Seattle, Washington, personal communication

For direct exposure to leachable/diffusible constituents of treated wood, salmon are most likely to be exposed during their residence and migration in freshwater and during their residency along shorelines and in estuaries. Once in the open water of the sounds or ocean, the exposure to diffusible constituents and associated risk from treated wood installations is reduced drastically and the primary route of exposure to these contaminants is through the food web. The open water feeding behavior of juvenile and adult salmonids limits their exposure to treated wood contaminants to those that occur in their food chain. For all practical purposes, “open water” exposure has lower risk when compared to the exposure that may occur during freshwater migration and residence time in estuaries.

The organic and trace metal constituents of treated wood tend to associate with the sediments and are usually associated with the fines and organic components of sediment. By their selective breeding behavior in well flushed cobble and gravel, the potential exposure of eggs and larvae to treated wood constituents associated with sediments is minimal. One exception could occur where salmon would spawn in close proximity to treated wood installations in a stream and the embryo/larval life stages could be exposed to leachable/diffusible constituents carried by inter-gravel flow.

Most direct exposure will occur in freshwater and estuaries when salmon are migrating near treated wood installations or if juvenile fish are drawn to nursery areas where treated wood installations are located. Indirect exposure results from the ingestion of food organisms exposed to treated wood preservatives. Because treated wood preservatives ultimately accumulate in sediment, benthic-based food webs have a greater potential for exposure to treated wood preservatives than plankton-based food chains.

Because juvenile salmon are more open-water fish as compared to bottom dwelling species, it is assumed that their exposure to sediment-bound contaminants is lower than that associated with benthic life histories. That paradigm should not be construed that exposure to sediment bound contaminants in estuaries is insignificant or without impact. Varanasi et al. (1993), in an assessment of exposure to Chinook salmon residing in contaminated estuaries, compared stomach and tissue burdens of aromatic hydrocarbons, polychlorinated biphenyls, and chlorinated pesticides in juvenile fish collected from the estuaries with hatchery fish collected in the rivers upstream of the estuaries and at other non-contaminated estuarine sites. Concentrations in stomach content and tissue burdens were clearly elevated in fish collected from contaminated locations (Duwamish waterway and Puyallup River/Commencement Bay estuary) compared to hatchery fish and uncontaminated estuaries.

Measurements of survivorship of fish collected from the estuaries, biomarker enzyme assays, the presence of hepatic DNA adducts with organic contaminants, *in vivo* and *in vitro* immunocompetence assays, and tissue burdens of contaminants support the position that estuarine exposure to contaminants poses a substantive risk to juvenile salmon. It is not always possible to separate or partition effects to specific groups of contaminants, hence there is no direct link to creosote treated wood (PAH). This study clearly demonstrates the importance and difficulty in assessing the impact of multiple contaminants and cumulative impact assessment.

One unique aspect of indirect exposure involves the initiation of exposure and accumulation of contaminants in the “microlayer” in estuarine and marine ecosystems and subsequent transfer into the marine food web. The microlayer is enriched in metals and organics by two to three orders of magnitude over levels in the water column. Buoyant particle matter scavenges the contaminants from the water column, but not all the contaminants are likely sorbed to particles. There is a great amount of fatty acids and other natural organics in the microlayer and some contaminants partition into these components. The chemistry and physics of the system is governed by the layered structure of the organics and the surface tension of the water. The microlayer may also receive contaminants from the air as well as the water column. The microlayer persists under wave action in up-to 6-foot waves. There is considerable information to suggest that the contaminants present in the microlayer are more toxic than the water column in industrial areas (Hardy et al. 1985, 1987a,b). The extent that contaminants released from treated wood (over-water and in-water) would accumulate in the microlayer is unknown.

Treated Wood – Diffusion and Leaching

When new treated wood is installed in aquatic environments, there is an immediate release of preservative material into the water column. For creosote treated wood, the release of PAH is a long term and continuing process (Brooks 1994a). Bestari et al. (1998) noted that releases of creosote from sections of BMP piling in large 12000-L microcosms peaked at 7 days and then declined to background levels after 84 days. The wood is saturated with creosote and over time, the material diffuses out into the water column. Pilings over 40 years of age still contain diffusible amounts of creosote that migrate from the product into the environment (Vines et al. 2000). Creosote treated wood has been routinely used in pilings in marine, estuarine, and some coastal river installations in Washington. However, permitted installations are presently managed under a memorandum of understanding (DE/WDFW 1995).

In comparison, the treatment of wood with the CCA Type C and AZCA treatments results in a product that will leach metals for a shorter duration and then for all practical purposes, the leaching decreases significantly. The metals that comprise the treatment process literally become fixed to the wood. For AZCA treated wood pilings, this occurs within ten days in freshwater or saltwater (Brooks 1995). AZCA treated wood may be used for in-water and over-water structures in Washington State. For CCA treated wood immersed in water, metal loss appears more protracted and may extend well past 21 days (Brooks 1994b). Leaching of metals is a function of pH with leaching rates increasing with decreased pH (Warner and Solomon 1990), however, the influence of buffers used to moderate pH in these studies may also have influenced leaching rates. Leaching generally increases when pH falls below 7.0 for copper, chromium, and arsenic in CCA treated southern yellow pine. Hingston et al. (2001) recently provided a comprehensive review of CCA treated wood leaching rates. They concluded that the initial high rates of leaching reported by Warner and Solomon (1990) were due to chelation with the citrate buffer. The impact of increased leaching rates due to increase acidity was not nearly as dramatic as originally indicated by the earlier studies. CCA Type C treated wood products are generally

used for land or over water structures in Washington State. For both treatments, copper is the primary concern for toxicity when compared to the other metals used as preservatives.

The preceding paragraph deals principally with treated wood pilings. Treated dimension lumber is often times incised and wood grain patterns afford a different surface that may result in different leaching rates for contaminants. Preservative retention and leaching rates may vary. Another variable is the quality of wood used. Soft woods (Douglas fir, southern yellow pine on the east coast) are preferred because of their retentive properties. Sometimes specific sections of wood will reject the preservative. Additional information on the applicability of types of wood for treatment can be obtained from the American Wood Preservatives Association (AWPA 1996).

Last, installation of treated wood products can result in other forms of exposure. Above water structures are exposed to greater temperature extremes, sunlight, and depending on the application, physical abrasion of the product. Holes drilled into the product during construction may introduce sawdust into the environment that, due to increased surface area, may exacerbate the release of preservative. While leaching studies characterize the migration of preservatives following immersion in water, the leaching of preservatives in above water structures may extend well beyond the times associated with immersed wood. Other aspects of treated wood installation (used of plated hardware, cutting and drilling) can also introduce contaminants into the aquatic environment.

This assessment is broken down into two major product groupings: 1) Creosote treated wood, and 2) metal treated wood. Within the metal treated wood section, both CCA Type C and ACZA treated wood are evaluated. These two treatments have been grouped together because copper is the limiting toxic constituent in leachates and there is a general paucity of environmental data for ACZA treated wood.

Biological Accumulation

Accumulation of contaminants in aquatic biota can occur by several mechanisms: direct adsorption across gills or skin, ingestion from food or water, and inadvertent ingestion of contaminated sediment. Bioaccumulation encompasses the accumulation of a contaminant in an organism from all these routes. Bioaccumulation can be contrasted with the term bioconcentration, which in some circles, specifically addresses uptake from water. This distinction is not always captured in published articles and reports. A third process that appears frequently in environmental literature is the term biomagnification. Biomagnification is a special condition where the accumulation of a contaminant tends to be progressively higher in higher trophic levels such that the highest concentrations appear in the upper trophic level predators. There is evidence that biomagnification may occur in highly chlorinated pesticides, polychlorinated biphenyls (PCB), and organic mercury, however, outside of these specific cases involving highly lipophilic compounds, biomagnification is rare. Organisms tend to regulate metals to a prescribed level and when exposure exceeds the physiological ability to deal with the

metals, toxicity occurs. As summarized by van Brummelen et al. (1998), biomagnification of PAH does not occur. A major reason for this is that gastro assimilation rates are low (range from 2 to 32% in mammal studies) and appear to decrease with increasing molecular weight and complexity (number of rings). The induction of metabolizing enzymes by biota also prevents the continued accumulation of PAH. After the PAH become transformed, they are excreted before they can accumulate to higher levels. Meador et al. (1995) recently reviewed the bioaccumulation of PAHs by marine organisms.

Metals are also subject to metabolic regulation and with the lone exception of methyl mercury, do not demonstrate biomagnification.

Key Studies

State and Federal agencies have made fair progress in the development of environmental criteria for water and sediment for the toxic constituents associated with treated wood. However, these criteria are under review and revision as new information becomes available. This review will focus on key critical studies that support this initiative in two ways. First, recent studies that provide additional guidance for establishing water and sediment criteria for the key toxic constituents of treated wood will be reviewed. The second critical area consists of studies that specifically address the environmental impacts associated with the use of treated wood and its impact on freshwater and marine environments. Review documents that capture much of the early supporting toxicological and exposure information were used to evaluate sediment and water quality criteria and benchmarks.

This review will not delve into the historic literature, but will rely on review documents to capture the earlier work and establish an assessment baseline for treated wood that is framed around existing criteria and more timely studies. Chronologically, these studies generally will have been published within the last 10 years. Most of the research specific to treated wood has focused on creosote treated wood and CCA-Type C treated wood. Outside of the review by Brooks (1995), only one study was found that examined the effects of field deployed ACZA treated wood in aquatic environments (Brooks 2000b, Lebow et al. 2000). Where the direction of this review requires review of literature on the toxicity and environmental fate of specific contaminants, those efforts have also focused on reference documents as opposed to specific research publications. However, recent research that contributed to the basic understanding of fate and toxicity of treated wood contaminants was actively solicited and reviewed.

Creosote Treated Wood

Creosote used as a wood preservative is a distillate of coal tar produced by high temperature carbonization of bituminous coal. The material consists of liquid and solid aromatic hydrocarbons and up to 3% tar acids and a lower percentage of tar bases. A listing of the more common PAH compounds is presented in Table 1. Present Best Management Practices (WWPI/CITW 1995) specify pressure treating and loading and post treatment procedures to recycle excess preservative and minimize environmental exposure to migration of preservative constituents. Post treatment procedures include a vacuum process to recover excess preservative, steaming the products for 2-3 hours at 212° to 240°F maximum, and a second vacuum treatment for 4 hours. Additional excess creosote is removed by an expansion bath treatment by heating the wood to 10-20°F above the pressurized treatment temperature and a vacuum treatment of 22” for a minimum of two hours. This assessment will focus primarily on wood products treated with creosote for the installation in marine and estuarine environments. Creosote treated pilings may also be found in estuarine portions of coastal rivers and in the lower Columbia River.

Table 1. Relative percentage PAH composition of creosote

PAH	Number of Rings	EPRI (1995)
Low Molecular Weight PAH		
Naphthalene	2	11.05
1- methylnaphthalene	2	6.8
2- methylnaphthalene	2	11.05
Biphenyl	2	6.8
Acenaphthylene	2	NV ^a
Acenaphthene	3	3.4
Fluorene	3	6.8
2,6- dimethylnaphthalene	2	3.4
Anthracene	3	11.05
Phenanthrene	3	11.05
2,3,5- trimethylnaphthalene	2	NV
1- methylphenanthrene	3	NV
High Molecular Weight PAH		
Pyrene	4	0.85
Fluoranthene	4	3.4
Chrysene	4	1.7
Benzo(a)anthracene	4	NV
benzo(e) pyrene	5	NV
benzo(a) pyrene	5	.85
Perylene	5	NV
dibenzo(a,h) anthracene	5	NV
benzo(a) fluoranthene	5	NV
benzo(k) fluoranthene	5	NV
benzo(g,h,i) perylene	5	NV
indeno(1,2,3-c,d)pyrene	6	NV

^a No value

This section discusses creosote toxicity and environmental standards for PAH in water and sediment. Impacts of creosote treated wood to the water and sediment depends on how readily creosote diffuses from treated wood products into the water column, hence the next section addresses migration rates of PAH from treated wood. The last portion of this chapter addresses recent key studies, primarily field studies of creosote treated wood installations, but also studies that may have bearing on eco-toxicological benchmarks in water and sediment. These studies consist of peer reviewed literature, gray literature, and draft reports. Neilson (1998) has prepared a very thorough review of the chemistry and biological effects associated with PAH in the environment.

Microbial Degradation of PAH

There have been numerous studies of the microbial degradation of specific PAH compounds and complex mixtures like creosote. Verschueren (1983) summarizes some of the early studies and provides estimates of biological and environmental half-lives for a number of individual PAH. Germain et al. (1993), Brooks (1994A), and Goyette, D. and K. Brooks (1998, 2000), provide general summaries of biodegradation and Neilson and Allard (1998) have provided a comprehensive assessment of microbial processes and PAH metabolism. A comprehensive review of this literature is well beyond the scope of this white paper. The following comments briefly summarize the general fate of PAH in the aquatic environment.

The lower weight PAH (2-3 ring structures) are generally more soluble and biodegradable than the heavy 4-6 ring structures. Metabolism may involve the substitutions of sulfur, nitrogen, or oxygen entities. When deposited in sediments, the presence of oxygen greatly facilitates microbial degradation. Temperature is a key environmental variable and warm environments will result in increased microbial activity and degradation of PAH compared to cooler or cold environments where PAH are much more persistent in anoxic environments (Eisler 1987). Biodegradation half-lives of PAH in water range from 12 hours (naphthalene) to 5.2 years (pyrene). Goyette and Brooks (1998, 2000) provide information on the fate of PAH released from creosote pilings into sediments and the changes in sediment concentrations as PAH diffuses from piling dolphins and become incorporated into marine sediments (discussed on p 30).

With respect to creosote treated wood, it is often noted that a sheen will float off of newly treated pilings when install or initially immersed in water. This sheen will be dissipated by dissolving of PAH into the water, volatilization of the more volatile low weight PAH, and possible incorporation into organic constituents in the microlayer. Microbial activity will also degrade PAH in the water column and microlayer.

Toxicity of Creosote Treated Wood to Aquatic Organisms

Creosote contains numerous constituents that are toxic to aquatic organisms. Creosote is composed primarily of polycyclic aromatic hydrocarbons (PAH; about 65 to 85%), with smaller percentages of phenolic compounds (10%), and nitrogen- sulfur- or oxygenated heterocyclics (EPRI 1995, Brooks 1994a). Creosote treated utility poles may also contain 1% pentachlorophenol, however, pentachlorophenol is not included in poles treated for marine application. To fully assess the risk associated with creosote treated wood, it is necessary to evaluate exposure mechanisms and dose response relationships of those toxic constituents associated with exposure. Lower molecular weight PAH (2-3 ring structures) are more soluble than the higher molecular weight PAH (4-6 ring structures). The composition of PAH in treated wood (relative to creosote) changes over time as a function of wood treatment processes, weathering in the field, differences in PAH solubility, and diffusion rates from treated wood. Changes in the composition of PAH associated with treated pilings in marine environments overtime have been documented by Goyette and Brooks (1998, 2000). Changes in the composition of PAH have also been observed in marine settings, railroad ballast, and in PAH associated with oil spills (Goyette and Brooks (1998, 2000, Brooks 2000c, Short and Heintz 1997). Toxicity information on pure PAH compounds (e.g., fluoranthene) has limited value in assessing the combined effects of all the constituents present in creosote treated wood.

There have been numerous reviews prepared on the toxicity of PAH and creosote treated wood (Johnson 2000, van Brummelen et al. 1998, Brooks 1994a, 2000c, Germain et al. 1993, Eisler 1987). The general mode of effect associated with acute exposures to PAH is non-polar narcosis (van Brummelen et al. 1998). Other major effects include biochemical activation/adduct formation (carcinogenesis), phototoxicity (acute and chronic exposure), and disturbance of hormone regulation. The role of PAH in endocrine disruption is not well documented. van Brummelen et al. (1998) did not specifically identify immunotoxicity as a mode of PAH toxicity, but it is an area that has been investigated (Varanasi et al. 1993, Karrow et al. 1999). This evaluation will only briefly touch on the nature of toxicity of PAH to plant and animal life. Readers are directed to seek out the referenced material for more detailed information about PAH toxicity.

Carcinogenesis

PAH have induced tumors in laboratory animals exposed by inhalation and ingestion (Germain et al. 1993) and the potential for carcinogenesis arising from exposure to creosote cannot be discounted in aquatic organisms. Most laboratory studies involve extended exposure of relatively high concentrations of specific PAH (e.g., benzo(a) pyrene). Specific PAH require metabolic activation to become carcinogenic (de Maagd and Vethaak 1998). The presence of hepatic (liver) tumors in sole, a benthic marine fish, has been linked to PAH contamination in sediments collected from industrialized areas around Puget Sound (Johnson 2000, Meyers et al. 1990, Stein et al. 1990, Krahn et al. 1986). Carcinogenesis in aquatic organisms is an endpoint of concern for exposure to creosote. As with other modes of toxicity, exposure conditions (i.e.

concentration of the contaminant, route and length of exposure) are critical to assess the carcinogenic potential associated with environmental exposure to creosote treated wood.

Hepatic carcinogenesis in fish parallels carcinogenesis in mammalian systems (i.e., a multistage process of initiation, promotion, and progression). In general, mammals and birds have greater biotransformation rates of PAH than fish (de Maagd and Vethaak 1998). Fish have greater rates than invertebrates. Induction of transformation enzymes in invertebrates exposed to benzo(a)pyrene have been studied in blue crab (Lee 1986) and bivalves (Anderson and Angel 1986, Broman et al. 1990). There are overlaps in measured biotransformation rates of PAH between major phylogenetic groups. Exposure to PAH as well as other xenobiotic compounds can induce the synthesis of biotransformation enzymes and thereby increase the production of carcinogenic metabolites. Consequently, parent PAH compounds are not specifically carcinogenic, rather carcinogenicity is attributed to metabolic intermediates of parent compounds (de Maagd and Vethaak 1998). This is important because other contaminants can stimulate these enzymes that then interact with PAH to form compounds that bind with nucleic acids or proteins (adducts). Biotransformation of PAH has been measured in the gastro-intestinal tract, heart, kidney, and gills of fish, so it is not entirely restricted to the liver. Generally, high molecular weight PAH (4 or greater rings), have more potential for transformation than low molecular weight PAH (≤ 3 rings). In one respect, it is somewhat ironic that the biochemical means for detoxification and ultimately excretion of PAH is the same path that leads to carcinogenicity. Factors influencing carcinogenesis included the age at time of exposure, genetic variation, nutritional status, growth rate, nutrient and non-nutrient modulators of carcinogenesis, and water temperature during initiation and or growth.

To summarize, specific PAH are likely to produce mutagenic and teratogenic effects in specific biological test systems. There is a growing body of information on mutagenic, teratogenic, and carcinogenic effects of PAH in aquatic organisms to complement the data on mammalian systems. A detailed assessment of these effects is outside the scope of this review. This review will look at efforts to use these type of effects to establish sediment or water quality benchmarks for the protection of aquatic resources.

Phototoxicity of PAH

Exposure of PAH to ultraviolet light creates free radicals and oxidized intermediates. These intermediates are more water soluble and potentially toxic. Photooxidation has been shown to increase the toxicity of crude fuel oil and fog oil (Larson et al. 1977, Poston et al. 1988). Others have studied photooxidation of specific PAH and effects on aquatic organism (e.g., Oris and Geisy 1985, 1987), but little is available about the specific influence of ultraviolet light on creosote. Schirmer et al. (1999) evaluated the effect of ultraviolet irradiation on creosote and subsequent exposure to trout gill cell cultures. Creosote was irradiated for two hours at an intensity of 53 μ watts UV light per cm^2 and was described as an “environmentally relevant” exposure. Subsequent exposures of cell cultures to UV-dosed and control creosote revealed about a 35-fold increase in cytotoxicity in cell cultures.

Immunotoxicity

There is limited information addressing the immunotoxicity of creosote to aquatic organisms. Karrow et al. (1999) reported depression of biological indicators indicative of immune function in rainbow trout that had been exposed to liquid creosote in microcosms. Effects included pronephros leukocyte (i.e., anterior kidney cells) oxidative burst, the number of sIg+ peripheral blood leukocytes, plasma lysozyme levels and a slight decrease in blastogenesis (cell reproduction) in cultures exposed to a lipopolysaccharide mitogen. The authors extrapolated a LOEC of 0.6 µg/L total PAH. These are all *in vitro* assays and it is difficult to extrapolate how they collectively influence immuno-competence of individual fish.

Immunological function was evaluated in juvenile Chinook salmon collected from contaminated waterways around Puget Sound and compared to upriver hatchery fish (Varanasi et al. 1993). The immunological studies were complimented with stomach and tissue analysis of the test fish for contaminants. Fish from the Duwamish Estuary and the Commencement Bay/Puyallup River estuary had elevated concentrations of PCB and aromatic hydrocarbon present in body tissues and stomach contents compared to the reference fish from hatcheries located upstream on the Green and Puyallup rivers. Tests of humerol and cellular mediated immunity indicated suppression in the fish collected from the estuaries. The experimental methods used in these studies involved artificial challenges of antigens (suppression of antibody production – humerol response) and a reduction in plaque forming cells. These studies clearly demonstrate an impact to immune function.

The biological assays did not assess the ability of the fish to resist natural exposure to infectious disease. What is needed is an assessment of the ecological significance of immuno-suppression. Is the degree of suppression relevant to the ability of the fish to defend itself against a natural viral, bacterial, or protozoan disease, or is it an artifact of a magnified response resulting from the artificial antigenic challenges used by the investigators? With respect to creosote treated wood issues, both PAH and PCBs make up the majority of sediment bound contaminants associated with the study's estuaries and it is not explicitly clear as to which if not both of these contaminant groups is responsible for the observed biological responses. These questions aside, the point remains that immuno-suppression was observed and in the context of cumulative impacts, is a viable concern for those fish that utilized the contaminated urban water ways during their migration to sea.

Acute Toxicity of PAH

Acute toxicity tests address short-term exposure to relatively high concentrations of a toxicant under controlled laboratory conditions. The general mode of effect associated with acute exposures to PAH is non-polar narcosis (van Brummelen 1998). The response is additive and can be evaluated by converting concentrations of multiple PAH from a gravimetric expression (µg/g) to a molar expression (µmole/g) and summing. Acute narcotic effects generally occur around 2 to 8 µmoles/gram wet weight (McCarty et al. 1992). Depending on the toxicants environmental chemistry, acute toxicity data may have only limited application for assessing environmental exposure. Controlled laboratory exposure conditions are rarely duplicated in

natural aquatic environments; i.e., photoperiod, temperature, pH, dissolved oxygen, feeding patterns etc. vary in natural environments. Consequently, acute toxicity test results are most useful for making comparisons of relative toxicity of different toxicants and bounding the breadth of toxic responses in aquatic organisms. For aquatic organisms, acute toxicity is established in test of generally 48 to 96 hrs, sometimes up to 168 hrs (7 days).

Most applicable toxicity testing for aquatic organisms has been conducted with specific PAH compounds rather than creosote. Some PAH compounds are considerably more toxic than others. Toxicity summaries have been prepared by Germain et al. (1993) and Brooks (1994a). Generally, acute test results are reported as the LC₅₀ for a specified exposure period. The LC₅₀ is defined as the concentration of a toxicant that is lethal to half of the experimentally exposed organisms. Acute endpoints ranged from a 48-hr LC₅₀ 5 µg benzo(a)pyrene/L for *Daphnia magna* to 1000 µg naphthalene /L (cited in Germain et al. 1993). The 72-hr LC₅₀ concentration for bass embryos was 240 µg naphthalene/L. These data indicate the potential toxicity of individual constituents present in creosote, but do not allow for assessing the combined toxicity of all PAH that may diffuse from treated wood.

Chronic Toxicity of PAH

Chronic toxicity is defined as the assessment of adverse effects that occur following extended exposure to a contaminant at concentrations that are not acutely lethal or are manifested in some other biological response.

Germain et al. (1993) also summarized chronic toxicity test results for several freshwater organisms. The lowest observed effect concentrations (LOEL) for fluorene was 430 µg/L where the chronic endpoint was emergence of chironomid larvae over 30 days of exposure. Fecundity in *D. magna* was reduced 44% at 125 µg fluorene /L in a 14-day test. A 23-day LC₅₀ for juvenile rainbow trout was 110 µg naphthalene/L. In comparison, a 90-day LOEC for survival in rainbow trout embryos exposed to phenanthrene was 8 µg/L.

PAH are toxic to aquatic organisms at low concentrations for sustained continuous exposure. The difficulty in applying these laboratory test results to real world exposures is that the release of PAH into natural bodies of water from treated wood (i.e., environmental exposure) differs significantly from the methods used to introduce pure compounds into essentially sterile laboratory exposure chambers. Environmental exposure is dependent on the age of the treated wood, methods used to treat the product, a host of environmental parameters, and the dilution afforded by the receiving body of water. Basic environmental conditions are controlled in laboratory toxicity tests, but are variable in the natural aquatic habitats where treated wood products are installed. Consequently, environmental exposure concentrations vary.

Environmental Standards for PAH

A benchmark is a concentration of a contaminant that indicates a biological response in association with some element of environmental exposure. Benchmarks carry an advisory capacity as compared to standards that are embodied in government regulations. Benchmarks have been proposed to help assess environmental impacts where standards do not exist and where existing standards are under review. The hazards and risks associated with creosote in aquatic habitats are under great scientific debate and standards that do exist under heavy scrutiny. The assessment of environmental impacts associated with treated wood depends heavily on the use of benchmarks for assessing potential impacts of treated wood. Because of the complexity of creosote and the number of PAH present, it is practical to assess impacts of creosote treated wood installations based on total PAH measurements and benchmarks. Benchmarks have been proposed (as discussed below) for individual PAH compounds, groupings by size (low molecular weight PAH and high molecular weight PAH), and total PAH. Additionally, the European community has proposed a benchmark based on biomarkers in fish.

Water

There are no benchmarks or regulations for total dissolved creosote in surface water, either marine or freshwater, as identified in state or federal regulations (WAC- 173-201A-040 and 40 CFR 131.36). Alaska has a water quality standard of 10 µg/L total aromatic hydrocarbons (AH) that includes mono-cyclic hydrocarbons. As a highly complex mixture of highly variable multiple-ringed organic compounds, it should be no surprise that a standard for total dissolved PAH has not been adopted. Lack of a promulgated criterion should not be viewed as an impediment to this assessment. Dissolved PAH becomes an issue for treated wood installations where dilution and turnover of water is low and the amount of installed treated wood is high. These conditions could lead to toxic conditions for aquatic organisms. Two approaches are evaluated with respect to establishing benchmarks for PAH in the water column. One is the direct, empirical comparison of the dissolved concentration of a PAH to aquatic toxicity test endpoints. The other is the application of the toxic unit concept to a listing of PAH present in creosote. As discussed in subsequent sections, field monitoring of treated wood structures suggests that the potential for toxicity of dissolved PAH associated with treated wood structure is generally low. The greatest risk for water column impacts most likely occurs when new pilings are installed (when sloughing of residual preservative occurs and diffusion rates of PAH are highest). Risk decreases with time as diffusion rates diminish.

Empirical Toxicity Test Results

From this standpoint, water quality benchmarks for specific PAH can be estimated from the data for pure compounds. While dated, Germain et al. (1993) provide an excellent overview of freshwater and marine toxicity testing in an eco-toxicological perspective for selected groups of PAH (Table 2). The eco-toxicological endpoint provided by Germain et al. (1993) is the lowest concentration listed for each constituent that they reviewed that had a significant biological effect (Germain et al. 1993). These results are based on toxicity tests of single compounds. The addition of creosote to water will result in a partitioning of hydrophobic oils and truly dissolved PAH. It is not well understood how the partitioning of individual PAH compounds is influenced by the presence of other dissolved PAH compounds and the presence of un-dissolved micro-

droplets in the water column. In practical terms, the values in Table 2 can be used as benchmarks for assessing potential adverse impact associated with individual PAH.

Table 2. Comparison of eco-toxicity threshold concentrations ($\mu\text{g/l}$) for PAH compounds (data from Germain et al. 1993)

Compound	Ecotoxicity Threshold ($\mu\text{g/l}$)
Naphthalene	10
Acenaphthylene	60
Fluorene	125
Anthracene	6.6
Phenanthrene	8
Pyrene	91
Fluoranthene	38
Benzo(a)anthracene	5
Benzo(a) pyrene	5
Benzo(k) fluoranthene	0.2

Toxic Unit Approach

A toxic unit concept can be applied in an additive model for assessing impacts from creosote, but that model is based on an assumption that all PAH compounds will remain dissolved up to their solubility limits and their solubility will not be influenced by the presence of other dissolved PAH and micro-droplets of PAH. Moreover, application of these toxicity results do not take into account the influence of microbial degradation, physical degradation, photo-oxidation and the likely increase in solubility and possible changes in toxicity associated with these processes that may occur to PAH present in the water column.

To assess the potential for any one constituent to exceed the eco-toxicological endpoints proposed by Germain et al. (1993), the proportion of each constituent in creosote should be determined, the leaching rate of creosote identified, and based on the water body that is impacted, a theoretical concentration estimated. A toxic unit calculation can be performed to estimate potential toxicity using the eco-toxicity benchmarks in Table 2. Swartz et al. (1995) and Swartz (1999) provide a method for implementing a toxic unit calculation for sediments that can also be applied to the PAH dissolved in the water column (NMFS 1998). For complex mixtures like creosote, this is a more sound approach that relying on the benchmarks of individual PAH compounds. Application of the toxic unit approach has been applied to railroad ties and leachates in ballast (Brooks 2000c). Measured concentrations of PAH in ballast were below toxicity thresholds for individual compounds and as total PAH. Assessments of water column impacts should be performed where currents or tidal flushing are low and the amount of creosote treated wood is high.

Sediment

Assessment of sediment toxicity has been a high priority initiative in regulatory and environmental resource management circles for several years. This interest has spawned several

different methods for assessing sediment toxicity. The following discussion will attempt to briefly summarize these efforts and arrive at an approach for dealing with assessing the risk associated with creosote treated wood.

The Washington State Department of Ecology has listed Sediment criteria for marine environments (WAC 173-204-320). The State standards (Table 3) were based on marine amphipod toxicity tests and do not address other ecological processes such as bioaccumulation and species differences to toxicants. However, the standards are a “narrative rule” that included both numerical criteria and biological testing criteria. Provisions for freshwater sediments are addressed in a reserve section of the regulation that defers to site specific assessments. When applied with other programs (e.g., Dredged Material Management Program and the Model Toxics Control Act [MTCA]), the standards can address a range of potential impacts on a site or project specific basis. Interactions with other environmental stressors that may interact on an additive or synergistic basis are not addressed in the direct application of the sediment standards to a specific situation. Site-specific considerations need to be addressed when applying these standards to the installation of treated wood structures. These include bulk criteria for low molecular weight PAH (LPAH – 2-3 rings structures) and high molecular weight PAH (HPAH – 4-6 ring structures). Bulk and individual PAH are expressed on mg per kg organic carbon (Table 3). Conversions have been made to provide the criteria based on three levels of organic carbon on a dry weight basis sediment. Johnson (2000) has proposed a total PAH threshold of 1.0 mg/kg dry wt. based on a 2% total organic carbon content in the sediment. This endpoint was based on data collected for hepatic carcinogenicity in sole and can be compared to a value of 2.0 mg/kg (1% TOC) proposed by the National Marine Fisheries Service (NMFS (1998) for the protection of salmon and their prey. This recommendation may over estimate risk because the analysis did not account for the contribution of other carcinogenic compounds in the sediment, although it is accepted that PAH are the most likely causative agent of hepatic lesions. Additionally, other possible elements of exposure to PAH during the early life stage (microlayer exposure of eggs/larvae) and near shore residence in potentially more highly contaminated areas could have contributed to the incidence of lesions that were attributable to PAH in the sediments where the fish were sampled (see p 28).

There have been numerous approaches to establishing sediment quality benchmarks standards for PAH. Jones et al. (1997) summarized ecological benchmarks as criteria for sediments for two classifications of PAH (low molecular weight and high molecular weight PAH) and individual PAH compounds (Table 4). The highest threshold benchmark is the EPA Office of Solid Waste and Emergency Response effects range-low (ER-L) value of 4000 µg total PAH/kg (Jones et al. 1997). The ER-L is based on sediment Eco-toxicity Thresholds (ET) derived using the equilibrium partitioning method. It is based on the lower limit of the 95% confidence interval as the ET, rather than the central tendency value, to maintain an appropriate level of conservatism for screening purposes. The other “threshold level” benchmarks were the Ministry of the Environment (2000 µg/kg), Region IV EPA (1684 µg/kg), and NOAA (4022 µg/kg). These benchmarks are normalized to 1% TOC. The range of these threshold benchmarks as influenced by changes in TOC is relatively large.

Table 3. Washington State Sediment Quality Standards – Marine Criteria

Constituent	Standard mg/kg Organic Carbon	Adjusted Standard based on % TOC (mg/kg bulk sediment dry) ^a			
		0.5 Percent Organic Carbon	1.0 Percent Organic Carbon	1.5 Percent Organic Carbon	2.0 Percent Organic Carbon
LPAH	370	1.85	3.7	5.55	7.4
Naphthalene	99	0.495	0.99	1.485	1.98
2- methyl naphthalene	38	0.19	0.38	0.57	0.76
Acenaphthylene	66	0.33	0.66	0.99	1.32
Acenaphthene	16	0.08	0.16	0.24	0.32
Fluorene	23	0.115	0.23	0.345	0.46
Anthracene	220	1.1	2.2	3.3	4.4
Phenanthrene	100	0.5	1	1.5	2
HPAH	960	4.8	9.6	14.4	19.2
Pyrene	1000	5	10	15	20
Fluoranthene	160	0.8	1.6	2.4	3.2
Chrysene	110	0.55	1.1	1.65	2.2
Benz(a)anthracene	110	0.55	1.1	1.65	2.2
Benzo(a) pyrene	99	0.495	0.99	1.485	1.98
Dibenzo(a,h)anthracene	12	0.06	0.12	0.18	0.24
Total benzofluoranthenes	230	1.15	2.3	3.45	4.6
Benzo(g,h,i)perylene	31	0.155	0.31	0.465	0.62
Indeno(1,2,3-c,d)pyrene	34	0.17	0.34	0.51	0.68

^a The adjusted standard for a PAH in a bulk dry weight sediment (e.g., 3.6 mg fluoranthene/kg sediment dry wt.), containing 2% TOC is determined by the following relationship: 3.6 mg/kg sed x 1.0/0.02 organic carbon = 180 mg/kg organic carbon. Consequently, the State standard was exceeded.

Table 4. Sediment benchmarks (NOAA and Florida) for individual, low molecular weight, high molecular weight, and total PAH (Jones et al. 1997) ^a

Constituent	NOAA		FDEP	
	ER-L	ER-M	TEL	PEL
Acenaphthene	16	500	6.71	88.9
Acenaphthylene	44	640	5.87	128
Anthracene	85.3	1100	46.9	245
Benz(a)anthracene	261	1600	74.8	693
Benzo(a)pyrene	430	1600	74.8	693
Crysene	384	2800	108	846
Dibenzo(a,h)anthracene	63.4	260	6.22	135
Fluoranthene	600	5100	113	1494
Fluorene	19	540	21.2	144
2-methyl naphthalene	70	670	20.2	201
Naphthalene	160	2100	3406	391
Phenanthrene	240	1500	8607	544
Pyrene	665	2600	153	1398
LMW PAH	552	3160	312	1442
HMW PAH	1700	9600	655	6676
Total PAH	4022	44792	1684	16770

^a All values are µg/kg dry wt., TOC not specified

Swartz (1999) provides an excellent review of this subject and provides a total PAH standard normalized to organic carbon content of the sediment based on toxic unit summation. As a consequence, scientists often refer to these earlier versions of sediment quality guidelines (Jones et al. 1997) which adds to the confusion of comparisons between benchmarks and assessing risk of PAH in sediments.

Swartz (1999) has generated three sediment guidelines for marine sediments based on concentrations of 13 PAH compounds: a threshold effect concentration (TEC - 290 µg/g organic carbon), a median effect concentration (MEC – 1,800 µg/g organic carbon), and an extreme effects concentration (EEC – 10,000 µg/g organic carbon). Conversions of Swartz’s TEC have been made over a range of 0.5 to 2.0 % organic carbon (Table 5). These proposed sediment guidelines, formulated under the toxic unit approach and consideration given to existing sediment benchmarks, provide a practical benchmark for assessing PAH contamination resulting from the installation of creosote treated wood structures. These guidelines are more conservative than the Washington State standards and the TEC approaches the level proposed by Johnson (2000) based on liver disease in flatfish. All these benchmarks and guidelines are for practical purposes, similar. Moreover, a standard based on total PAH concentrations is more applicable to the complexity of creosote treated wood installations.

Table 5. Proposed standards by Swartz et al. (1999) based on TOC values normalized to organic carbon extrapolated to a range of sediment TOC levels

SQG (Swartz 1999)	(mg total PAH/kg organic carbon)	Sediment Guideline (µg/kg bulk sediment dry wt.)			
		0.5 Percent Organic Carbon	1.0 Percent Organic Carbon	1.5 Percent Organic Carbon	2.0 Percent Organic Carbon
Threshold	290	1.45	2.9	4.35	5.8
Median	1800	9	18	27	36
Extreme	10,000	50	100	150	200

The toxic unit approach has been criticized by van Brummelen et al. (1998) because of the assumption that a similar mode of action can not be applied to all PAH. Given that some PAH are clearly carcinogenic following transformation while others are not, some are much more persistent than others, and toxicity varies over several orders of magnitude from one PAH to another, the criticism has some merit. However, the authors note that no viable alternative is available to collectively evaluate the risk of PAH contamination in sediments. While there is room for uncertainty in the toxic unit concept, as applied, it may prove very functional for regulatory and compliance purposes.

Biomarkers

Potentially adverse exposure to PAH may become biochemically manifested in fish as enzyme systems are induced to metabolize the PAH (van Brummelen et al. 1998). This response forms the basis for the consideration of three biomarkers within the European environmental community that would indicate potentially hazardous exposure to PAH. These biomarkers are:

1) cytochrome-450-1A, an enzyme that is induced by exposure to large molecular weight PAH as well as polychlorinated hydrocarbons and dioxins; 2) bulky aromatic-DNA adducts (the product of enzymatic transformation of PAH); and 3) the presence of PAH metabolites in bile. These endpoints may be considered as simple evidence that the organism is responding to and possibly dealing with exposure to a contaminant(s) with no measurable impact to that organism or population. Application of biomarkers as regulatory endpoints was considered in Europe under the precautionary principle in the interests of providing an adequate margin of safety. There presently is no initiative in the State of Washington to incorporate biomarkers into a regulatory framework.

Avoidance

Exposure to dissolved oil or suspensions of oil into the water column may interfere with the olfactory organs in fish leading to behavior effects. This potential effect is most frequently associated with oil spills. Oil sheens (usually dominated by lower molecular weight PAH) are frequently observed with newly installed creosote pilings. Goyette and Brooks (1998) hypothesized that releases of creosote from treated pilings occurs in the form of microdroplets. There have been no specific studies, either laboratory or field studies, that have specifically demonstrated an impact to fish olfaction as a result of creosote treated wood placed in aquatic environments. Studies of crude oil exposure on coho (Nakatani and Nevissi 1991) and Chinook salmon (Brannon et al. 1986) have evaluated the impacting on homing behavior in salmon. In both studies, one-hour exposures to high concentrations of crude oils and dispersed crude oils did not change the percentage of migrating salmon that returned to their spawning area or the amount of time it took to reach the spawning area. These studies suggest that exposure to creosote sheens or dispersions are not likely to affect homing behavior of salmonids exposed *in situ*.

The potential for impacts should be addressed on a site-specific basis where migrating salmonids may be exposed to newly installed creosote treated wood. Impacts are most likely when residual preservative may wash off of treated wood and should decline with weathering of the installation.

Diffusion Rates of PAH from Creosote Treated Wood

Any attempt to estimate the potential impacts of creosote treated wood in aquatic habitats will require an estimate of the amount of material that will diffuse into the water column. Brooks (1994a) reviewed much of the available literature on the leaching of PAH from treated wood. Most of these leaching rates have been derived from small- to moderate-scale closed laboratory systems by Ingram et al. (1982). Some of the leaching rates were also derived from treated wood samples that were not prepared under existing best management practices. Brooks used his assessment of migration rates to develop a risk assessment model that is based on estimating leaching rates and consequently exposure. Brooks based his models on salinity, temperature, piling age, and treatment retention. For Douglas fir pilings treated to 25 pcf and installed in salt

water (30 ppt) at 12° C, Brooks used a leaching rate of 17.3 µg creosote per cm² per day. This compares to a range of measured leaching rates in salt water for yellow pine from 7 to 39 µg creosote per cm² per day at 30 ppt (Ingram et al. 1982 as cited by Brooks 1994a). Total PAH loss rates vary from less than 10 µg/cm²/day in cold marine environments to >50 µg/cm²/day in warm freshwater environments (Brooks 1994a). Generally, Douglas fir is used for the preparation of creosote treated pilings in the Northwest.

Bestari et al. (1998) evaluated the leaching of creosote derived PAH from Douglas fir pilings treated to a retention of 9.1 kg/m³ of marine grade creosote. Pilings were placed in 12,000 L microcosms for 84 days. Concentrations of PAH were measured in water and in sediment trays over the duration of the study. Each microcosm had treatments of 0.5, 1, 2, 3, 4, and 6 treated pilings. Each microcosm (except the 6 treated piling microcosm) had additional untreated pilings added so that each microcosm had a total of 6 pilings. Total PAH concentrations in the water column peaked at 7 days and declined to background levels at 84 days. Estimated loss rates for PAH were 50 µg/cm²/day. The highest reported concentration of total PAH was about 100 µg/L in the 6-piling treatment at day 7.

Other factors besides diffusion rates will also influence the introduction of creosote from treated wood into bodies of water. Portions of pilings above the water line and over-water structures constructed of treated wood are exposed to higher and more variable temperatures. Heating and cooling, and the corresponding expansion and shrinkage of treated wood may influence the rate of removal of creosote from treated wood. Accumulations of preservative on the surface of the piling or timber may fall into the water, may be rinsed into the water by precipitation, or may be rinsed into the water by maintenance activities on the structure (e.g., hosing down a dock). Abrasion of treated wood may also introduce fragments of treated wood into a body of water. Brooks reports of finding drilling waste from the installation of a bridge constructed of treated wood in at Horseshoe Bayou (Brooks 2000a). Information is not available to quantify these possible sources of input into aquatic systems. Inadvertent releases such as these are manageable by conducting operations in an environmentally conscious manner, others are more susceptible to the whims of nature.

The assessment of toxicity associated with creosote treated wood will address toxicity of leached constituents in the water column, toxicity of leached constituents that accumulate in sediment, and toxicity to organisms that come in direct contact with the treated wood product.

Key Studies

This section will summarize recent studies that address the environmental impacts of creosote treated wood use in the aquatic environment. The studies focus on field evaluations of treated wood structures or summary studies of potential effects and environmental concentrations of PAH. One limitation of most field studies is that none of them focus on large treated wood installations. Metropolitan water fronts that sustain shipping, docking, commercial business and industry will have a much greater level of installed treated wood than recreation or industrial sites

that are removed from metropolitan areas. Uncertainty about estimating potential impacts of treated wood installations increases as the amount of treated wood increases beyond the levels associated with these reviewed studies.

Creosote Effects on Herring Reproduction

Vines et al. (2000) conducted field and laboratory investigations on the effects of creosote treated wood on egg-larval development in Pacific herring (*Clupea pallasii*). Biological endpoints that were monitored included embryonic development, embryo cardiac function, embryo movement, hatching success, and morphology of larvae. Laboratory exposures were static systems. Salinity was also evaluated as an environmental variable in the toxicity tests. The laboratory tests involved exposures of aged creosote treated wood, fresh kiln dried Douglas fir (untreated) and no-wood control treatments. Static exposure solutions for treated wood were prepared by incubating 1 gram of aged (40+ years) treated wood from a marina in California to 200 mL of 16 ppt filtered seawater.

The authors report an LC₅₀ for hatching success at 0.05 mg/L (nominal concentration) of creosote in static exposure systems; statistically significant reductions in hatching success became apparent at ca. 0.009 mg/L (nominal concentration). In the laboratory, the adverse effects of creosote treated wood were most pronounced on embryos adhering to the treated wood surface (0% survival to hatch). Non-attached embryos had delayed development in 40-50 % of the exposed population. Embryonic heart rates measured from day 5 through day 9 post fertilization decreased from a mean level of about 50 beats/min to a rate less than 10 beats/min. at day 9. The control responses, which consisted of a non-treated wood and a “no-wood” treatment, increased from 92 and 97 beats/min at day 5 to 127 and 130 beats/min at day 9. The surviving creosote treated embryo’s displayed severely arrhythmic heart contraction patterns while both control treatment embryos had a steady rate of contractions.

Developing embryos exposed to creosote show erratic and increased body movements within the chorion (egg wall) when compared to the control treatments. Movements by embryos exposed to creosote were characterized as showing tremors and twitches. In comparison, patterns of the control treatment embryos consisted of less frequent and distinct tail and trunk displacements.

Hatching success was greatest in controls (89%), showed statistically significant reduction in the untreated wood (73%), and 9 % of free-floating eggs in the creosote treated wood exposure hatched. None of the eggs adhering to the treated wood hatched.

One-hundred percent of the treated wood embryos surviving to the time of hatch were abnormal. Observed responses were abnormal fluid retention in the visceral cavity (ascites), fluid accumulation around the heart (pericardial edema), and spinal curvature (scoliosis). Some of these abnormalities were also observed in the wood control treatment, and at a rate (20%) that was also significantly greater than the control rate of 8%.

The significance of this study is that those effects demonstrated in the laboratory under controlled conditions of exposure were also observed in field studies of herring eggs deposited on aged creosote treated pilings at Fort Baker, California. Herring eggs deposited on pilings treated with creosote did not hatch. This study identifies a potentially significant adverse impact (depending on what percentage of the herring stock spawn in this area) to a key food species for salmon. Herring in Puget Sound are a candidate species under ESA and represent a key link in numerous marine food webs. Consequently, the potential for significant adverse impacts increases with the amount of treated wood that may provide spawning habitat for herring in estuarine and marine waters. Creosote treated pilings are lethal to herring eggs that are deposited on the piling surface. The toxicity likely results from direct contact of the eggs with the treated wood. Other results of the laboratory phase of herring egg study are not directly extended to the field, in particular, the exposures associated with the static exposure system on un-attached eggs.

Prince William Sound Studies

In 1989, the supertanker Exxon Valdez ran aground in Prince William Sound creating one of the largest oil spills in United States history. Because of the location and the value of the ecological resources that were impacted, it is one of the most extensively studied environmental disasters on record. Weathered crude oil has lost the more water soluble and low molecular weight constituents leaving a globular mass of organic material that is dominated by PAH. There is very little in common between the mechanisms of exposure to weathered oil and treated wood installations other than the fact that the toxic constituents of each are dominated by a complex mixture of PAH. The value in looking at the work done following the Exxon Valdez oil spill are that this work has better defined ecotoxicological endpoints for complex mixtures of PAH. This work was reviewed from this perspective and it follows that applications of creosote treated wood that would result in similar concentrations and exposures of total PAH would have similar effects. For the most part, these are chronic exposures that have been evaluated in both field and laboratory studies. The toxic endpoints that have been reported in these studies may represent the most sensitive indicators of ecological stress posed by complex mixtures of PAH. In this regard, they reduce the uncertainty associated with the effects of complex mixtures and bridge the gap between the application of safety factors to laboratory acute and chronic endpoints and real world effects.

Bue et al. (1998) evaluated the mortality of pink salmon resulting from spawning in areas fouled with weathered crude oil from the Exxon Valdez oil spill. *In situ* embryo mortality was higher in beaches contaminated with weathered crude oil compared to non-contaminated beaches from 1989 through 1993. In 1994 and 1995, there were no differences of embryo mortality observed between the previously fouled beaches and un-fouled reference beaches. Gametes were collected from returning adults in 1993 (1991 year class) and 1994 (1992 year class) at both fouled and reference beaches and taken to the laboratory where eggs were fertilized and monitored. The embryos from the oil-fouled beaches in 1993 had greater mortality than the embryos produced from the reference beaches. In 1994, there were no differences attributable to location or location. The authors attributed the differences in the 1993 gametes to the parental stocks exposure to weathered crude oil as embryos in contaminated beaches in 1991.

Studies by Heintz et al. (1999) complement the field and laboratory observations of Bue et al. (1998) with controlled laboratory exposure of pink salmon embryos to: 1) weathered-oil covered gravel (direct contact), 2) aqueous extracts from weathered oil-covered gravel, and 3) exposure to aqueous extracts of gravel coated with *very* weathered oil. Embryo mortality and PAH accumulation in embryos in the direct contact and aqueous exposures studies of weathered oil were not statistically different. The authors interpreted this observation to mean that exposure of embryos was mediated by dissolved PAH and physical contact of weather oil was not a significant vector of exposure in the test systems. Concentrations of 1.0 µg/L total PAH from the very weathered oil was lethal where as the same concentration (1.0 µg/L total PAH) from the “weathered oil” was not toxic to salmon embryos. The aqueous exposure solution of the very weathered oil had a greater proportion of high molecular weight PAH when compared to the weather oil. The shift to higher molecular weight PAH in the very weathered oil was corroborated by analyses of PAH in the embryos.

Carls et al. (1999) evaluated the effects of dissolved total PAH in larval Pacific herring that were exposed as embryos and larval forms for 16 days. Exposure solutions were prepared by running seawater over gravel coated with weathered crude oil. Two exposures were conducted with the coated gravel to yield exposures with “less-weathered crude oil” and “more weathered crude oil”. Exposures to the more weathered oil resulted in physical malformations, genetic damage, inhibited swimming, decreased size and mortality at an initial concentration of 0.7 µg/L total dissolved PAH. Concentrations as low as 0.4 µg/L total dissolved PAH causes sub-lethal responses such as yolk sac edema and delayed maturity. The more weathered oil exposure solutions had a greater proportion of high molecular weight PAH than the less weather oil exposure solutions. The difference may account for the greater relative toxicity compared to the more weathered oil exposure test results. The authors report a lowest observed effect concentration (LOEC) of 0.4 µg/L total dissolved PAH.

To summarize, the studies of Heintz et al. (1999) and Carls et al. (1999) provide a foundation for establishing an ecological toxic benchmark of 0.4 to 1.0 µg/L total dissolved PAH based on developmental toxicity in cold water fish. Similarly, concentrations of total PAH dissolved in water from creosote treated wood could be expected to exert the same influence on aquatic life as what has been demonstrated with weathered oil.

Sediment Quality Threshold Study (Carcinogenesis)

A considerable amount of data has been collected from Puget Sound and other estuarine harbors addressing the prevalence of tumors in bottom dwelling marine fish and the potential association with PAH contamination in sediment. Johnson (2000) analyzed toxicological or pathological data for English sole (*Pleuronectes vetulus*) and the relationship with sediment PAH concentrations by using a “hockey stick” regression method. This is essentially the same information presented by Horness et al. (1998), but also includes data on DNA adducts and reproductive fitness endpoints. The method basically generates two regression lines, one encompassing “no effects levels” for pathological lesions and having a slope of “0”, the other one regressing the prevalence of liver lesions with increasing total sediment PAH concentrations

and having a significant and positive slope. Because PAH concentrations were log-normally distributed, the PAH concentrations were log transformed for the regression analysis. Where the two lines intersect essentially defines the threshold concentration where an increase in the effect variable occurs.

Several toxicological and pathological endpoints were evaluated including four levels of liver lesions, the formation of PAH-DNA adducts, and female sole reproductive fitness (three variables).

The incidence of four types of liver lesions were evaluated on fish 2 years old or greater. The lesions and their threshold concentrations in total sediment PAH ($\mu\text{g}/\text{kg}$ sediment dry wt.) were determined. The endpoints and their 90% confidence intervals were:

- | | |
|--|-------------------|
| ▪ Neoplasms (cancer) | 2,800; 11 to 5500 |
| ▪ Pre-neoplastic foci of alteration
(precursor to a neoplasm) | 54; <0 to 54 |
| ▪ Specific degeneration/necrosis (SDN)
(a special lesion leading to tissue death) | 940; 681 to 1200 |
| ▪ Non-neoplastic proliferative lesions
(rapidly growing non-cancerous growths) | 230; 1.4 to 830 |
| ▪ Any liver lesion | 640; 300 to 1000 |

The DNA-adduct analysis resulted in a threshold level of 290 $\mu\text{g}/\text{kg}$ PAH dry wt. and a 90% confidence interval of 6 to 1380.

There were data for three reproductive abnormalities in female English sole that were evaluated to estimate threshold effect levels for sediment PAH. Confidence levels were not calculated for these reproductive endpoints due to insufficient data. The individual reproductive endpoints were:

- | | |
|----------------------------|----------------|
| ▪ Inhibited gonadal growth | 4,000; no C.I. |
| ▪ Inhibited Spawning | 630; no C.I. |
| ▪ Infertile eggs | 630; no C.I. |

The authors also reviewed studies that indicate decreased growth in sole exposed to PAH-contaminated sediment and to sole fed a diet of food contaminated with PAH (Kubin 1997; Rice 1999). Johnson (2000) suggests a threshold for growth would occur between 2,000 and 4,000 $\mu\text{g}/\text{kg}$ PAH dry wt. The Rice study fed polychaete worms raised on sediment containing PAH (3000 to 4000 $\mu\text{g}/\text{kg}$ PAH dry wt.) to sole. Growth was significantly inhibited after 28 days of feeding.

A major concern (and one identified by the authors) is that other contaminants (polychlorinated biphenyls (PCB), chlorinated pesticides, and trace metals) that are also carcinogens were present in sediments and are a significant confounding factor (Johnson (2000)). The analysis has not factored the presence of these other contaminants into their regression analysis. However, Meyers et al. (1990) performed a logistic analysis on hepatic neoplasms that attributed 12.1 % of the incidence of lesions to total sediment aromatic hydrocarbons and was the most significant contaminant in the model. Other contaminants were polychlorinated biphenyls and chlorinated butadienes. The link between PAH exposure and hepato carcinogenicity is not in dispute, however, not accounting for exposure to other contaminants raises the potential for their threshold effects levels to over estimate the risk associated to PAH sediment concentrations.

A second issue was raised by Brooks (1999) that identified a concern for exposure to contamination prior to when the fish were sampled. Hepatic lesions require time to develop, so adult (2 year) fish were collected in deeper, offshore waters. Juvenile sole reside in shallow water nearer the shoreline and if they live near contamination hot spots, may have received a higher exposure to contaminants during the early portion of their residence than indicated by the concentrations in sediment that occurred where they were collected. Along this reasoning, sole eggs incubate at the surface and if spawning occurs near industrial development, those eggs may be exposed to contaminants in the micro layer. Hardy et al. (1987a) have demonstrated chromosomal aberrations and reduced hatching success in sand sole embryos exposed to surface microlayer water collected from urban bays. In both these instances, potential exists for higher exposures to contaminants than were associated with the sediments where the adults were collected in the Johnson (2000) analysis. Additionally, the embryo-larva and juvenile life stages of sole may be more susceptible to PAH exposure than adults.

In Johnson's (2000) concluding statement, the NMFS recommends a threshold level of 1000 µg/kg PAH dry wt., or for a 2% total organic carbon content in Puget Sound sediment, a concentration of 50 mg/kg total organic carbon. The 1000 µg/kg total PAH concentration is not a recommended sediment guideline for protection of salmonids, but was the estimated level at which PAH-related effects on marine bottomfish would be minimal. Other sediment contaminants may have influenced the biological endpoints of sole in this study. The proposed threshold accounting lower than the sediment level recommended by Swartz (1999) and is an issue that requires further study for resolution.

Sooke Basin Study

In 1995, a field study was initiated in the Sooke Basin, Vancouver Island, to evaluate the environmental impacts associated with the installation of creosote treated piles (Douglas fir) in a marine basin (Goyette and Brooks 1998). The study design included the installation of three dolphins constructed with six piles each. The pilings were installed in an area of the basin with a slow current of ~1.89 cm/sec in a general east to west direction. A mechanical "untreated pile" control was built with six untreated Douglas fir piles. The primary experimental dolphin was constructed with six creosote treated piles that were treated to Best Management Practices (BMP) standards as established by the wood treatment industry (WWPI/CITW 1995). Sampling

intensity was greatest around the BMP dolphin. A secondary treatment was the installation of a six-pile dolphin of 8-year old weathered creosote-treated piles. An open control site with no dolphins was also identified. The orientation of these treatments in an east to west direction was the open control site, 20 m to the untreated dolphin, 77 m to the BMP dolphin, and 70 m to the weathered dolphin. The study site was characterized prior to and at the time of installation of dolphins. Post-dolphin construction sampling was conducted at 14 days, 185 days, 270 days for a small select group of samples, 384 days, and 535 days. A great deal of data was collected to characterize and measure the impacts of the treated wood and releases of PAH into the environment. The concentration of PAH was measured in sediment and water, and in selected biota. Benthic fauna was evaluated in terms of abundance and diversity. Toxicity was assessed with bacteria luminescence for sediment pore water and solid phase (Microtox), amphipod sediment bioassays, and biological responses of penned mussels (*Mytilus edulis*).

An addendum to this initial report has been issued that summarizes additional sampling that was performed at 1360 and 1540 days post dolphin installation (Goyette and Brooks 2000). This additional sampling focused on the accumulation and persistence of PAH in sediments around the dolphins, the toxicity of the sediments, and the accumulation of PAH in mussel tissue. The key results of the Sooke Basin studies are discussed below and the reader is referred to the reports for additional detail.

Water Samples

Concentrations of PAH in water were determined at three locations associated with the BMP dolphin and the control location. PAH were collected on a semipermeable membrane device. Total PAH were based on 15 individual PAH compounds. Total PAH concentrations were estimated at 13.4 ng/L at the control location and ranged from 17.9 to 30.8 ng/L at BMP dolphin locations. The individual concentrations of PAH were well below the eco-toxicology levels proposed by Germain et al. (1993) and based on a toxic unit calculation (0.00075) for acutely toxic endpoints, are well below levels that would be associated with other estimates of toxicity discussed elsewhere in this report.

Sediment accumulation of PAH

Background (pre-installation) concentrations of total PAH (TPAH) were 0.19 and 0.13 mg/kg dry wt. at the weathered and BMP stations, respectively. Increases in total TPAH in sediment (dry wt. basis) were observed at both the BMP and Weathered dolphin sites. At the weathered piling, sediment accumulations were evident 10 m down-gradient of the dolphin (0.94 mg/kg TPAH @ 384 days). The maximum sediment concentration was observed 0.5 m down-gradient (105 mg/kg TPAH @ 14 days). At 384 days, the concentration was 33.8 mg/kg TPAH. Elevated concentrations of PAH were also observed up-gradient of the weathered dolphin (ranged from 2.3 mg/kg on day 384 @ 2.0 m up-gradient to 0.49 mg/kg on day 384 @ 28 m up-gradient. For comparison, sediment accumulations were evident 10 m down-gradient of the BMP dolphin (0.40 mg/kg TPAH @ 384 days). The sediment concentration observed 0.5 m down-gradient (7.8 mg/kg TPAH @ 14 days). At 270 days, the concentration was 54.5 mg/kg TPAH. Elevated concentrations of TPAH were also observed up-gradient of the BMP dolphin

(ranged from 3.6 mg/kg on day 384 @ 2.0 m up-gradient to 0.8 mg/kg on day 384 @ 28 m up-gradient). The overall point here is that within the context of spatial and temporal variability, the releases of PAH by the weathered and BMP dolphins were similar with relatively lower levels associated with the BMP dolphin. The apparent spatial extent of impact to sediments from the BMP dolphin was estimated at 7.5 m and is based on a sediment increase of about a factor of ten above the baseline concentration of 0.13 mg/kg TPAH. Because less data (fewer sampling sites) was collected from the weather dolphin site, there is less certainty about estimating a spatial extent of impact.

In the follow-on studies, concentrations of TPAH had dropped from the highest observed concentrations at Day 384 (~30 mg/kg dry weight) to ~ 7 mg/kg dry weight (at days 1360 and 1540) in the top two cm of sediment beneath the BMP dolphin. The authors had expected concentrations to continue to increase rather than drop. The decrease in TPAH concentrations may be attributed to increased microbial metabolism, an influx of material from sedimentation processes (burial) of which a major component resulted from biological activity (i.e., feeding and waste from sessile biota found on the pilings), a change in the analytical laboratory that conducted the chemical analyses, a reduction in diffusion rates from the pilings, and a layer of sessile biota coating the pilings. The accumulation of biological material below the BMP has also increased the concentrations of hydrogen sulfide to potentially toxic levels.

Accumulation of PAH in biota

The accumulation of PAH was also determined over time in penned mussels (*M. edulis*) located 0.5 m down-gradient of the weathered dolphin, 0.5, 2.0, and 10.0 m down-gradient of the BMP dolphin, and at the open (no dolphin) control site. The initial concentration of PAH in the test population was 16.2 (± 2.2 [mean \pm 95% C.I.] ng/g wet wt.). Mean mussel tissue concentrations [\pm 95% C.I.] on day 14 were 68.1 [± 9.1] $\mu\text{g/kg}$ wet wt. @ 0.5 m at the BMP dolphin and 58.4 \pm 14.7 $\mu\text{g/kg}$ wet wt. @ 0.5 m for the weathered dolphin. The open control was 44.1 \pm 8.1 $\mu\text{g/kg}$ wet wt and was similar to concentrations measured at 2.0 and 10.0 m down-gradient of the BMP dolphin. Measurements at day 185 (mean range of 15.4 to 32.4 $\mu\text{g/kg}$ wet wt.) and day 384 (mean range of 8.3 to 15.5 ng/g wet wt.) were somewhat scattered around the sample site (non-systematically) and lower than the concentrations observed at day 14. To summarize, mussels tissue burdens indicated an increase over initial PAH concentrations at day 14 (including the control group) and a decline to baseline concentrations at day 384. Induction of PAH metabolizing enzymes may explain the lack of accumulation of PAH in subsequent sampling (Akcha et al. 2000, van Brummelen et al. 1998). Overall, there were no differences in mussel tissue concentrations at the control and dolphin installations. Consequently, it is difficult to relate any observed differences in biological response to empirically determined tissue burdens. The topic of relating tissue levels of contaminants to demonstrable adverse effects is an area of needed growth. The U.S. Army Corp of Engineers has taken an initial step with the creation of an Environmental Residues Effect Database (<http://www.wes.army.mil/el/ered>), however, there presently is not a lot of PAH data to populate this data base (ERED 2001). Last, as a point of reference, total PAH concentrations in marine bivalves collected from the Oregon coast in 1978-79 ranged from a low of 31.4 $\mu\text{g/kg}$ total PAH in caper clams (*Tresus capax*) collected in Coos Bay to 1324 $\mu\text{g/kg}$ total PAH in mussel (*Mytilus edulis*) collected in Yaquina Bay (Mix 1982).

Mussels that had attached themselves to the BMP piling were also sampled and analyzed for the presence of PAH at day 1540. Concentrations were below the limit of detection (20 µg/kg wet wt.), however, one sample indicated the presence of phenanthrene, fluoranthene and pyrene.

Biological Effects: Studies with mussels

A lot of discussion was presented regarding the biological response of mussels in the Sooke Basin study. As indicated above and also corroborated in evaluations of bioconcentration factors, condition factors, and further PAH concentration data for soft and gonadal tissue, the open control group of mussels showed comparable levels of PAH accumulation over time to the BMP and one WP treatment groups. This relationship was quite variable.

Despite the confounding effects of the tissue burden data, the gross biological responses of long-term survival and growth were systematic in mussels. From the start of the exposure through day 185, there were essentially no measured differences in survival at the open control, 0.5 m from the weathered dolphin, or at 0.5, 2.0 and 10 m down-gradient of the BMP dolphin. At day 384, mean survival ranged from 80% to 89% with no apparent relationship with distance from dolphins. Growth at day 384 (mean ± 95% C.I.), on the other hand, was highest in the open control group (69.5 ± 0.8 mm), lowest in the 0.5 m BMP treatment (59.3 ± 2.4 mm) and 0.5 m weathered dolphin treatment (64.2 ± 0.9 mm), then followed by the 2.0 (67.2 ± 0.7 mm) and 10.0 m (68.7 ± 2.1 mm) BMP dolphin treatments. The differences in growth between the control and the 0.5 m samples for both the BMP and weather dolphin were significant. The differences in mussel growth were also observed at day 185.

Mussel reproduction assays did not produce results that would point to a systematic relationship between control and treated wood treatments. Successful reproduction rates ranged from 79.8 to 83.3 % normal larvae at Day 185 and 65.3 to 89.9 % at Day 569 across all treatments.

Biological Effects: Sediment toxicity testing with marine amphipods

A large number of 10-day sediment toxicity tests were performed with two species of marine amphipods (*Rhepoxynius abronius* and *Eohaustorius washingtonianus*). A reference control sediment was obtained from Whidbey Island for *R. abronius* testing and from Esquimalt Lagoon for *E. washingtonianus*. Initial sediment tests for day 14 and day 185 were conducted with the entire contents of the sediment core sampler (10 cm depth). PAH characterization of the sediments had been based on samples representing the top 2 cm of sediment. By homogenizing the cores, the concentration of PAH in the upper two cm of the sample (where most of the dispersed PAH from the pilings was expected to occur) was diluted. Recognizing that this practice could dilute the PAH and bias the results, subsequent amphipod testing was based on sediment collected from the top two centimeters of the study area. The battery of amphipod toxicity tests were statistically analyzed and the following conclusions were drawn by the authors.

Survival of test organisms exposed to the Sooke Basin control location sediment and the mechanical (untreated piles) control sediment was statistically less than ($\alpha = 0.05$) the reference

control sites (Whidby Island and Esquimalt Lagoon) for each species. The authors note that Sooke Basin sediments do not support populations of marine amphipods. Survival at the untreated pile control site was also less than the open control site.

Survival in amphipods tested with sediment from the BMP site was reduced relative to the reference site and the Sooke Basin open control site, but amphipod survival of the BMP treatment was statistically ($\alpha = 0.05$) no different than survival at the Sooke Basin untreated dolphin location. Subsequent analysis of sediments collected at 0.0 and 0.5 m down-gradient of the BMP and untreated dolphin structures indicated that survival was statistically ($\alpha = 0.05$) lower at the BMP site when compared to the untreated piling control. There was no difference observed in amphipod survival for sediments collected from the 2.0 and 5.0 m distances from the test dolphins.

A similar battery of statistical tests was performed on the weathered dolphin sediments. Survival of amphipods at the weathered dolphin site was less than survival at the reference sediment sites and for the open control site in Sooke Basin. However, there was no difference between the weathered piling site and the untreated dolphin site for all tests and when partitioned by distance from the structure. Last, survival of amphipods exposed to sediments from the BMP site was lower than survival of amphipods tested with sediments collected at the weathered dolphin site irrespective of partitioning by distance.

The authors noted that fluoranthene and phenanthrene exceeded EPA marine sediment criteria for those sediments with significant amphipod toxicity. Amphipod toxicity was demonstrable in sediments collected from the upper two centimeters and within 0.5 m of the BMP structure. These results needed to be considered in light of the fact that Sooke Basin sediments do not support viable populations of the marine amphipods tested.

Sediment samples were collected for testing with *E. washingtonianus* at both day 1360 and 1540 from directly beneath the BMP dolphin, at 0.5 m, 2.0 m, 5.0 m, 10.0 m, and at a new location 20 m down-gradient. Sediments from the open control and the mechanical control (un-treated pilings at 0.5 m down gradient) were also tested. Amphipod toxicity test results were not significant for percentage survival for Days 1360 and 1540, however, there was decreased survival noted within 2.0 m of the BMP dolphin in some of the tests. Open control survival was 86 % and 93 % on Days 1360 and 1540, respectively. The reference sediment had 94 % survival. Hydrogen sulfide had built up to levels of 60 to 68 mg/L in the sediment (assumed interstitial water) and may have contributed to the observed toxicity.

Biological Effects: Microtox Results

Microtox is a bacterial assay that measures light output of a marine bacterium. Increased toxicity is inferred from decreases in light output. Tests were performed on pore water extracted from sediment samples and a solid phase test of the sediment. Results of the initial set of Microtox assays covering pore water and solid phase test were mixed with indications of toxicity at all locations including controls. Given that the open control locations were also toxic, little can be inferred from these assays. Results were normalized to open control and untreated

dolphin control for solid phase sediment testing. These results indicated some level of sediment toxicity within 0.5 m of the BMP dolphin, but no toxic effect associated with the solid phase tests of sediment collected from the weathered dolphin site.

Additional Microtox testing was conducted on Day 535. These results were compared to the untreated dolphin only, no open control samples were collected. Toxic conditions were indicated in sediments collected within 2.0 m of the BMP dolphin and beneath the weathered dolphin.

In the follow-up sampling, Microtox tests were performed on sediment samples collected on Day 1540 only. All liquid phase tests indicated toxicity at the BMP dolphin (Stations 0.0, 0.5 m, 2.0 m, 5 m, 10 m, and 20 m as well as the mechanical control (0.5 m). The open control site was not toxic. Much of the observed toxicity was attributed to the presence of hydrogen sulfide. Results for the solid phase Microtox tests paralleled the results of the liquid phase tests and indicated moderate toxicity for the six BMP sites (0.0 m to 20 m, inclusive) and mechanical control dolphin sediments. Sediment from the open control site was not toxic.

Biological Effects: Echinoderm fertilization Tests at Day 535.

Sea urchin fertilization tests were also performed at day 535. These tests indicated toxicity within 0.5 m and underneath the untreated, weathered, and BMP dolphins.

Biological Effects: Abundance

Several measurements of infaunal abundance were evaluated at the study locations (indices of diversity, abundance, dominate species). These included taxa richness, Pielou's Evenness Index, Shannon's Diversity Index and Margalef's Richness Index, as well as several statistical evaluations to assess relationships with relationships between TOC and PAH concentrations. The infaunal data was highly variable. There was a weak indication of decreased abundance when TPAH concentrations exceeded 10 mg/kg dry wt. at the BMP location. The abundance of some benthic fauna was positively correlated with sediment PAH. At the weathered dolphin, however, increased infaunal abundance was associated with increase PAH concentration. Sediment total organic carbon and percentage fines had a much greater influence on abundance. Differences between sediment TOC and percentage fines also confounded comparisons of abundance between the dolphin sites. The untreated dolphin had no apparent effect on the infaunal community. The author proposes a threshold concentration of 10 mg/kg TPAH for invertebrate abundance. A considerable amount of effort was expended and presented to assess infaunal abundance and readers with further interest are encouraged to review the document.

Summary of Sooke Basin Study

From one perspective, the Sooke Basin Study represents a fairly comprehensive field evaluation of treated wood effects in a marine environment. The study, with in its limitations, has provided a comprehensive basis for spatially quantifying the impacts of a six-piling treated wood structure. As the authors have concluded, the data presented sets an outer boundary of ~7.5 meters as a region of demonstrable impact. These impacts are manifested in the sediments,

however, the increases in PAH in “control” mussels located away from the structures raises questions. It is also uncertain as to how increased densities of pilings would influence sediment PAH concentrations and associated biological effects.

Subsequent sampling at day 1360 and 1540 indicated that concentrations of PAH in sediments had decreased and that accumulations of biological material beneath and adjacent to the dolphins had contributed to elevated hydrogen sulfide concentrations. The BMP pilings were photographed and were heavily colonized with mussels, sea anemones and other marine life. More marine life was associated with the BMP pilings compared to the mechanical control pilings and was attributed to the erosion and sloughing of the non-treated wood caused by borers and *Limnoria*. The BMP piling was heavily colonized with sessile organisms (mussels, sea anemones).

Based on existing Washington State sediment criteria, sediment concentrations of PAH were exceeded beneath and immediately adjacent to the dolphins during the initial phase (up through day 535) of the study. PAH concentrations were determined in the top 2 cm of the sediment column.

Microcosm Studies (University of Guelph, Ontario)

An array of eight 12,000-L microcosms were established to characterize the diffusion and fate of PAH in creosote treated Douglas fir pilings (Bastari et al. 1998). The pilings were treated to a retention of 9.1 kg/m³ marine grade creosote. Two of the microcosms received 5 untreated pilings as controls. The high treatment received 6 treated pilings. The remaining 5 microcosms received combinations of treated and untreated pilings bringing the total number of pilings in each microcosm to 6 pilings, but with experimental levels of 0.5, 1, 2, 3, and 4 treated pilings. The pilings were situated in a cluster in the center of the microcosm. The surface area of treated wood ranged from 2,286 cm² to 27,089 cm². The total surface area of all pilings ranged from 27,089 cm² to 27,223 cm². The duration of exposure was for 84 days with 10 sample days over the duration of study.

Each microcosm was inoculated with rooted and floating aquatic plants, phytoplankton, zooplankton, fish, invertebrates. No data was presented on concentrations of PAH in the biota or possible adverse biological effects.

Total PAH concentrations in the water column peaked at 7 days and declined to background levels at 84 days. Estimated loss rates for PAH were 50 µg/cm²/day. The highest reported concentration of total PAH was about 100 µg/L in the 6-piling treatment at day 7. The lower molecular weight PAH dominated the distribution of PAH in the water column.

Leaching rates have been discussed previously in this white paper. The most significant observation of this study is that there was no accumulation of PAH detected in sediment over the 84-day study. Sediment accumulation was monitored in sediment jars placed on the floor of the microcosms and away from the clusters of pilings. The microcosms were essentially static systems with mixing of water caused by wind or the biological activity of fish and invertebrates.

While concentrations of PAH peaked at 7 days and then declined to background concentrations by day 84, there was no increase in sediment concentrations. This observation suggests that PAH that diffuse into the water column are lost to surface evaporation, undergo degradation by photo-oxidation or microbial activity, or accumulate in biota. Adsorption on to plastics in the microcosms may also account for the fate of the PAH.

Many of the field studies addressed in this section identify sediment accumulation beneath and adjacent to creosote treated wood installations. Brooks (1998) hypothesized that loss of creosote from treated wood occurs as the shedding of dense micro-droplets that sink to the bottom where they accumulated in sediments. This mechanism could explain why PAH were not observed in the sample jars as there is no mechanism for “settled” PAH to contaminate the sediment jars. This also points to a transport mechanism analogous to the microlayer, only operational at the sediment water interface that allows currents to move dense materials along the point away from a point of deposition until they become incorporated into the sediment.

Risk Assessment Creosote Facility

A risk assessment of the McCormick and Baxter Creosote Treatment Site was performed to evaluate the risk associated with PAH contamination present in Willamette River sediments adjacent to the site (Pastorok et al. 1994). This facility manufactured creosote treated wood for many years. Maximum sediment concentrations resulting from the manufacture of creosote treated wood were estimated from a figure in the report and were normalized to 1.9% Organic Carbon (OC):

- LPAH 20 mg/g OC, HPAH 4 mg/g OC - Fish and crayfish habitat
- LPAH 23 mg/g OC, HPAH 13 mg/g OC - Clam habitat
- LPAH 240 mg/g OC, HPAH 72 mg/g OC - Nearshore shelf
- LPAH 400 mg/g OC, HPAH 400 mg/g OC - Beach

Mid channel and upstream reference sites were low (< 3 mg/g OC and < 0.036 mg/kg, respectively) and demonstrated little residual impact from the site. PAH were measured in resident fish (suckers). PAH are quickly metabolized in fish, and no statistically significant differences were observed PAH concentrations in fish tissue for samples from the site and the upstream location. No adverse effects were observed in suckers that are more intimately associated with benthic food webs and contact with sediment. These observations included no measurable effect on liver histopathology. Concentrations were reported as “low”. The authors noted that mobility of suckers may minimize exposure to the areas contaminated by creosote. They note that migrating salmonids would have a low potential for exposure to contaminated sediments during migration.

While acknowledging that resident crayfish may have a high potential for exposure, no data was presented on PAH concentrations that were found other to state that they were “low”. Actual sample data is summarized in the study’s final report and was not presented in the article.

Much of the risk assessment was based on threshold effects for *Hyallolela azteca* 10-day sediment toxicity tests. These tests indicate a threshold of LPAH at 21 mg/g OC, and for HPAH at 12 mg/g OC, and a benzo(a)pyrene threshold of 0.32 mg/g OC. The result for LPAH translates to 21000 mg/kg OC. The Washington State sediment standard is 370 mg/kg OC for LPAH. For HPAH, the Washington State standard is 960 mg/kg OC. The threshold for *H. azteca* is 12000 mg/kg. There is a large disparity between the threshold effect for *H. azteca* and the Washington state sediment (marine) guideline. It is not clear if the disparity can be explained by marine vs. freshwater species and ecosystems. It should be noted that the threshold effects levels were based on a reference site and required 25% mortality to be significant ($\alpha = 0.05$). This does not appear to be a very conservative measure for a 10-day static exposure test. Microtox tests also indicated toxicity within 300 ft of the shoreline.

The authors concluded that there was no evidence for adverse effects through out the main channel. They mention that there may be toxic effects for crayfish chronically exposed to PAH contamination and that acutely toxic conditions likely exist at the most contaminated sites. These sites had concentrations ranging up to 240 mg/g OC LPAH and 72 mg/g OC HPAH.

Field Deployed Sediment Study (EPA – Gulf Breeze)

Sediment was contaminated with marine grade creosote at nominal concentrations of 177, 420, and 844 $\mu\text{g/g}$ and used for exposures of natural seeded populations of marine organisms in portable exposure systems (Tagatz et al. 1983). One set of exposures was conducted in the field with the colonization provided by un-filtered seawater. The low concentration (177 $\mu\text{g/g}$) had lower overall abundance in the field laboratory exposures, but not in the laboratory series to tests. Colonization of several classifications of marine organisms was significantly inhibited at the low treatment. The low treatment concentration of 177 $\mu\text{g/g}$ is a relatively high concentration and impacts are not unexpected. Over the eight-week period of colonization, sediment concentrations of “creosote” in the mid-level exposure decreased by 30% in the laboratory exposure systems and 42% in the field deployed systems. The sand used in the exposures systems was 82% particles between 0.36 and 0.71 mm. No organic content of the sand was specified. The authors noted that diversity indices may not catch impacts to particularly sensitive species. The salient point of this study, however, is that it sets a benchmark of effects at the low exposure concentration of 177 $\mu\text{g/g}$. This has value as many of the reviewed field studies did not attain PAH concentrations in sediments that result in measurable population effects.

Indiana Bridge Studies

In 1997, the US Forest Service initiated a study of bridges constructed with creosote treated wood in the Midwest (Brooks 2000a). While bridges are not specifically identified as over water structures in this assessment, the study can provide valuable insight into the releases of contaminants into aquatic habitats. The Indiana bridges cross Pipe Creek in Cass County, Indiana. Pipe creek is located in a well-established agricultural area and farm practices have influenced the stream ecosystem and its biota as well as the indices used to assess impacts

associated with the bridges. The bridges were initially sampled in November 1997. A second sampling of sediment for toxicity tested was conducted in August 1998. The bridges were designated as a 2-year old bridge (#146 - constructed in 1995) and a 17-year old Bridge (#148 - constructed in 1980). Both bridges were constructed with 20 Class A pilings treated to a retention of 17 pounds per cubic foot (in the retention zone). Beams and planks were treated to a retention of 8 to 10 lbs creosote. Measure current velocities in Pipe Creek were 1.0 cm/s and 5.8 to 9.7 cm/s, respectively for #146 and #148. Discharge in Pipe Creek ranges from a daily mean low of 3.3 cfs to a high daily mean of 67.6 cfs. A number of physical and biological measurements were taken at the study sites to assess the impact of the creosote bridges on the stream.

Sediment Accumulation of PAH

At the 2-year old Bridge (#146), total PAH concentrations in sediment (2 cm sample depth) were below detection at a control site located 76 ft upstream of the bridge and 33 ft downstream of the bridge. Maximum concentration 5.5 mg/kg dry wt. was measured 6 ft downstream of the bridge. Concentrations 10 ft downstream were 1.7 mg/kg dry wt. Concentrations 20 ft downstream were 0.54 mg/kg. Concentrations of total PAH exceeded sediment tolerance levels ~1.5 ft downstream to ~ 10 ft downstream of the bridge when normalized to sediment carbon content (measured and reported as total volatile solids [TVS]). The author uses a mean of the Tolerance Effect Level and the Probable Effects Level proposed by Swartz et al. (1999) as a benchmark to assess risk.

At the 17-year old Bridge (#148), total PAH concentrations in sediment (2 cm sample depth) were below detection (<0.1 mg/kg dry wt.) at the upstream control site. PAH were measured 33 ft downstream of the bridge. The maximum concentration of 2.3 mg/kg dry wt. was measured 6 ft downstream of the bridge. Concentrations ranged from 0.98 mg/kg dry wt. under the bridge to 0.5 mg/kg dry wt. 33 ft downstream of the bridge. With consideration of sediment carbon content (based on a regression analysis of TOC and TVS), normalized concentrations of total PAH did not exceed tolerance levels downstream of this 17-year old structure.

Water

No measurements were taken of dissolved or diffusible PAH in water at Bridge 148.

Biological effects: Benthic Invertebrate Population Assessment

Biological effects were assessed by examining benthic invertebrate populations and sediment toxicity testing with the freshwater amphipod (*Hyalella azteca*).

Biological effects at both bridges were assessed with analysis of benthic invertebrate populations. Benthic invertebrate samples were collected at the sediment sampling locations and the different species were identified and counted to provide these calculations. The data was quantified in terms of overall abundance and in two indices: 1) Shannon's Index for diversity – richness, and 2) Pielou's Index for diversity evenness. Calculations of Shannon's Index range

from 0 to 3 with values ≥ 2 indicative of a healthy or un-impacted benthic ecosystem. Calculations of Pielou's Index range from 0.0 to 1.0. Values >0.5 are usually associated with a healthy or un-impacted benthic ecosystem. The assemblages of invertebrates have been influenced by past farming practices and invertebrates less tolerant of water and sediment quality changes caused by farming are generally absent and may influence indices of abundance and diversity measured at the study sites.

Bridge 146 (2 years post-installation). Shannon's index calculations ranged from 0.85 to 1.1. Pielou's index ranged from 0.35 to <0.5 . Both indices were on the low end of their reference scales where high values are 3.0 and 1.0, for Shannon's and Pielou's indices, respectively. Overall, there was no systematic relationship between these indices and sample site orientation with the bridge. Benthic invertebrate abundance was lower upstream of the bridge than downstream. The invertebrate populations were dominated by oligochaetes (segmented worms) and chironomid (midge fly) larvae. There were fewer mayflies, caddis flies and stoneflies. Generally, mayflies, caddis flies and stoneflies are associated with "cleaner" streams and midge fly larvae (particularly those of the genus *Chironomus*) and oligochaetes are associated with more organically enriched systems. Overall, the invertebrate analysis was inconclusive. There was no indication of obvious impact that could be attributed to the 2-year old bridge. The authors note that there was some apparent reduction in abundance related to increased PAH concentrations above sediment guidance levels (Swartz 1999), but this observation was not statistically significant.

Bridge 148 (17 years post installation). Shannon's index calculations ranged from 0.55 to 1.1 downstream of the bridge. The highest index was 1.23 at the upstream control site. Pielou's index ranged from 0.23 to ~ 0.4 and was highly correlated with Shannon's Index values. Both indices were on the low end of their reference scales where high values are 3.0 and 1.0, respectively. Overall, there was no systematic relationship between these indices and sample orientation with the bridge or sediment PAH concentrations. Overall benthic invertebrate abundance was lower upstream of the bridge than downstream. The invertebrate populations were dominated by oligochaetes and chironomid larvae. There were fewer mayflies, caddis flies and stoneflies. Generally, mayflies, caddis flies and stoneflies are associated with cleaner streams and midge fly larvae (particularly those of the genus *Chironomus*) and oligochaetes are associated with more organically enriched systems. Overall, the invertebrate analysis was inconclusive. There was no indication of obvious impact that could be attributed to the 17-year old bridge.

Biological Effects: Sediment Toxicity Test

Sediment toxicity tests performed on sediments collected in November 1997, were invalidated by unacceptably high control mortality in the test population. Sediment toxicity tests were performed on sediments collected in August, 1998 from the same sites originally sampled in November 1997 (i.e., the upstream control site, and at sampling locations at 1.5, 6.0 and 33 ft downstream). A laboratory control was also included in the experimental design. It is unclear if the sediment fractions used in the amphipod toxicity test was that sediment associated with the upper two cm or a mixture of the entire sample that was collected. No supporting PAH

chemistry or characterization was performed on the August 1998 sediment samples because the toxicity test results were negative.

Bridge 146 (2 years post-installation). Sediment for toxicity testing was collected in August 1998 and evaluated with amphipod bioassays. The responses in the control treatment were acceptable and the survival rates associated with the upstream control location and the three downstream locations were high with no statistical differences among treatments. There was no chemistry performed on the August 1998 sediment samples, consequently, it is unknown what levels of PAH were present in the August sediments that were tested.

Bridge 148 (17 years post installation). The initial battery of tests performed on sediment samples collected in November 1997 were invalidated due to an unacceptable rate of mortality in the control treatments. Sediment for toxicity testing was collected in August 1998 and evaluated with amphipod bioassays. The response in the control treatment was acceptable and the survival rates associated with the upstream control location and the three downstream locations were high with no statistical differences among treatments. There was no chemistry performed on the August 1998 sediment samples, consequently, it is unknown what levels of PAH were present in the August sediments that were tested.

Summary of Creosote Bridge Study

The studies of the two bridges on Pipe Creek did not indicate any overt impacts to the biota. Sediment guidelines were exceeded at the 2-year old bridge (#146) and there was a marginal indication of impact related to invertebrate populations, however, this could be attributed to randomness. No adverse biological effects were observed at the site of the 17-year old bridge (#148), nor was there any indication that sediment total PAH concentrations exceeded guidance levels.

South Carolina DNR Studies

The South Carolina Department of Natural resources conducted several studies addressing potential impacts of primarily CCA Type C treated wood in coastal environments, however, in the initial phase of the study, sediments and oysters were analyzed for 12 PAH (Wendt et al. 1996). The field study was conducted at ten high-density dock sites (each with a corresponding reference location) located within the Charleston Harbor estuary and associated creeks. Reference sample sites (without docks) were selected to match salinity, tidal flux, and basic geomorphometry with their corresponding dock sites. Sampling “zones” at each treated wood site were established at <1 m from the dock, > 10 m from the dock, and at the reference station. The number of docks constructed with creosote treated wood was not specified.

Sediment contamination

The study characterized the fine grain component of sediments, but did not conduct analyses for TOC. Mean Sediment PAH concentrations were not statistically different between the near dock

site (<1 m), distant sampling sites (>10 m) sampling sites, and the no dock reference locations. Sediment concentrations ranged from 690 (\pm 294 standard error [s.e.]) $\mu\text{g}/\text{kg}$ dry wt. at >10 m to a high mean concentration at the reference site of 1180 (\pm 324 s.e.) $\mu\text{g}/\text{kg}$ dry wt. The mean concentration at <1 m was 978 (\pm 346 s.e.) $\mu\text{g}/\text{kg}$ dry wt.

Oyster PAH concentrations

Resident oysters (*Crassostrea virginica*) were also sampled and analyzed for PAH. As was observed in the sediment results, mean concentrations of PAH in dried oyster tissue were not significantly different among the three sampling zones. The maximum mean concentration was observed at the <1 m zone [3550 (\pm 1070 s.e.) $\mu\text{g}/\text{kg}$ dry wt.]. The mean concentrations at the >10 m zone and reference location were 2060 (\pm 1640 s.e.) $\mu\text{g}/\text{kg}$ dry wt and 2170 (\pm 1960 s.e.) $\mu\text{g}/\text{kg}$ dry wt., respectively.

Biological Effects: Microtox

Solid phase Microtox tests results (EC_{50} – light reduction) did not indicate any difference among the three zones. There was a significant positive correlation noted, however, between EC_{50} values and total PAH concentrations at specific dock locations. This suggests at a minimum that the Microtox bacterium (*P. phosphoreum*) is not adversely affected by PAH, at least in the concentrations associated with the solid phase Microtox testing.

Summary

There was no adverse effects associated with PAH contamination in this study. The study did not identify how many docks were constructed with creosote treated wood, but the fact that sediment concentrations at the reference locations exceeded the dock locations suggests that at least some of the docks were constructed with creosote and that creosote was fairly uniformly distributed about Charleston Harbor and associated tidal tributaries.

Metal-based Treated Wood

Two types of metal-based treated wood are addressed in this assessment of over-water and in-water structures: ACZA and CCA Type C treated wood. These treatments are usually applied to Douglas fir or western Hemlock in the Pacific Northwest. Additional information on applications and loading rates are available from AWPA (1996).

ACZA

Ammoniacal copper zinc arsenate treated wood involves fixation of an aqueous solution of 25 % zinc as zinc oxide (ZnO), 50% copper as cupric oxide (CuO) and 25% arsenic as arsenic pentoxide (As₂O₅) (AWPA 1996). Wood is treated by either the Bethel (full cell) or Lowry (empty cell) process. The Lowry process is the preferred method for aquatic applications of treated wood. Post-fixation is achieved by air seasoning, kiln drying (160-170 °F), or in-retort ammonia removal with in-plant holding (WWPI/CITW 1995). Preservative retention levels have decreased with refinements in production and the adoption of Best Management Practices. In 1995, marine pilings were set to 40 kg/m³ (Brooks 1995). Presently, ACZA retention for marine applications is now 24 kg/m³ (1.5 pounds per cubic foot (pcf)) and it is 16 kg/m³ (1.0 pcf) for freshwater piling. AWPA (1996) provides current specifications for pilings and dimensional treated lumber.

CCA Type C

Chromated copper arsenate treated wood involves fixation of an aqueous solution of 47.7 % chromate as chromium trioxide (CrO₃), 18.5% copper as cupric oxide (CuO) and 34% arsenic as arsenic pentoxide (As₂O₅) (AWPA 1996). Once impregnated with preservatives, fixation is achieved by several processes including air seasoning, kiln drying, steaming, or hot water baths, depending on the type of wood and fixation process. Depending on the wood and intended uses, treatment and loading will vary. There are three types of CCA treated wood (A,B, and C). Type C consists of the formulation above and is most commonly used for applications around water. Much of the environmental research on CCA Type C treated wood has been performed on southern yellow pine in the eastern half of the United States and Canada. Marine applications require retention rates from 24 to 40.7 kg/m³ (1.5 to 2.5 pcf).

This section discusses metal toxicity and environmental standards for copper, chromium, arsenic, and zinc in water and sediment. Impacts of metal based treated wood to the water and sediment depends on how readily trace metals leach from treated wood products into the water column. The last portion of this chapter addresses recent key studies, primarily field studies of metals based treated wood installations, but also studies have may have bearing on eco-toxicological benchmarks in water and sediment.

Metal Toxicity

Numerous evaluations have been performed on leaching of metals from CCA Type C and ACZA treated wood. In both types of wood, it is generally understood that copper has the greatest potential for toxic effects. A large body of research exists for copper, chromium, zinc, and arsenic that has been used to establish water quality guidelines based on acute and chronic toxicity of these metals to aquatic organisms. The establishment of sediment guidelines for these metals, however, is less clear-cut and will be addressed in more detail.

All of these metals exist in sediments and to a much lower degree in the water column at background concentrations. The bio-availability of these metals in the water column is influenced greatly by existing water quality. Copper and zinc exist as divalent cations and water quality standards in freshwater are based on total hardness. Meyer (1999) evaluated the relationship of LC₅₀ values for five transition metals and concluded that the existing regression based equations may overestimate toxicity when water hardness exceeds 200 mg/L. Hydrogen ion (pH) has a major influence on the chemical speciation of Cu in freshwater systems with in the pH range associated with most healthy aquatic ecosystems (6.0 to 9.0). As pH levels approach 7.0 and become more acidic, the percentage of ionic copper (Cu²⁺; the toxic form of copper) relative to total copper increases. Copper forms complexes with dissolved organic carbon, carbonate and hydroxides (Meador 1991) that are considered less toxic than the dissolved divalent cation. The influence of pH on zinc speciation is less dramatic.

Meyer et al. (1999) have proposed a biotic-ligand model that explains the toxicity of copper and nickel to fathead minnow based on the gill bound fraction of the metals. The model presents a more predictive model for acute toxicity when compared to free-ion activity over a 19-fold range of water hardness. Applicability of these models to sub-lethal and chronic toxicity was not discussed.

Arsenic and chromium are present as anions (negatively charged compounds) and their toxicity is not as greatly influenced by hardness. Consequently, hardness is not included in the derivation of water quality standards. Arsenic is present in the As V (5⁺ valence state) as arsenate pentoxide (As₂O₅) in freshwater and marine habitats, however, arsenate can in certain situations be reduced to arsenite (As III: 3⁺ valence state -As₂O₃). Generally, arsenite is considered more toxic than arsenate and is a carcinogen. Chromium is present in the Cr VI (6⁺ valence state) as chromate, but can also be reduced to the 3⁺ valence state (Cr III). Cr VI is the most mobile and toxic form of chromium in aqueous systems. The fixation of chromium in the treated wood process results in the reduction to the 3⁺ valence state and reduces the potential for leaching and mobilization.

In this assessment, all metals associated with treated wood are evaluated.

Water Quality Standards

The water quality standards used for this assessment are chronic water quality standards as formulated in the Washington Administrative Code (WAC 173-201A-040) and represent the dissolved fraction of the metal. These standards are compared to reported leaching rates of metals found in CCA and ACZA treated wood (Table 6). Some basic conclusions from this comparison point to the relative risk of each metal preservative.

Table 6. Comparison of leaching rates and freshwater and marine chronic water quality standards

Metal	Chronic Standard ^a	CCA Leaching Rates		ACZA Leaching rates	
		Warner 1990; Brooks 1994 (µg/cm ² /day)	Ratio chronic standard:leaching rate	Worst case Leaching rate (µg/cm ² /day)	Ratio chronic standard:leaching rate
Freshwater (100 mg/L hardness)					
Cu	6.3 µg/L	1.62	3.89	85.11	0.02
Zn	57 µg/L	NA	NA	0.04	1520
Cr III	110 µg/L	0.52	212	NA	NA
Cr VI	11 µg/L	0.52	21.2	NA	NA
As V	190 µg/L	8.39	22.7	0.099	1920
Marine Chronic Water Quality Standard (30 ppt Salinity)					
Cu	3.1 µg/L	2.6	0.84	10.67	0.29
Zn	81 µg/L	NA	NA	2.16	37.5
Cr III	NA	NA	NA	NA	NA
Cr VI	50 µg/L	0.12	416.67	NA	NA
As V	36 µg/L	1.09	33.03	0.10	364

^a WAC 173-201A-040

In both freshwater and marine systems, copper is the most toxic (lowest water quality standard) of the four metals considered. When chronic water quality criteria are compared to leaching rates for each metal (as a ratio), copper has the lowest ratio indicating greater potential risk. For CCA treated wood, the relative rank for risk is Cu>Cr>As in freshwater and Cu > As > Cr in seawater. For AZCA treated wood, the ratios are Cu>>Zn>As in freshwater and Cu>Zn >As in seawater. These are generic comparisons that only serve to illustrate relative risk.

Comparatively, the risk (WQS:leaching rate) associated with copper in CCA treated wood (southern yellow pine) is less than the risk associated with Cu in ACZA treated wood (Douglas fir), however, the relative risk associated with arsenic in CCA treated wood is greater than the risk associated with arsenic in ACZA treated wood. Initially, copper leaching rates from AZCA are considerably larger than rates associated with CCA treated wood. In both cases however, leaching rates in immersed treated wood drop off to very minute levels in a matter of days for both methods of treatment.

Response of Salmonids to Metals

The chronic water quality criteria for copper, chromium, arsenic and zinc are protective for salmon. The most sensitive life stages are swim-up and early juvenile stages and given the relatively low chronic water quality standards for copper, chromium and zinc, these three metals are the most likely to exert toxic effects on salmon. Chapman (1978) provided some of the more definitive studies for the toxicity of copper and zinc in chinook salmon and steelhead early life stage tests. Test results were expressed as the LC₁₀ concentrations over 200 hours of continuous exposure. The LC₁₀ expresses the concentration that will impact 10 % of the test population. Tests were performed in soft water (hardness = 22 mg/L CaCO₃).

- Copper. The most sensitive life stages for exposure of steelhead were parr and smolt where the LC₁₀ concentrations were 8 µg/L and 7 µg/L copper, respectively. For chinook salmon, the most sensitive life stages were alevin and swim-up stages where 200-hr LC₁₀ concentrations were 15 and 14 µg/L. The calculated chronic water quality standard at 22 mg/L CaCO₃ hardness is 3.2 µg/L.
- Zinc. The most sensitive life stages for exposure of steelhead were swim-up and parr where the LC₁₀ concentrations were 53 µg/L and 61 µg/L zinc, respectively. For chinook salmon, the most sensitive life stages were swim-up and smolt stages where 200-hr LC₁₀ concentrations were 68 and 170 µg/L. The calculated chronic water quality standard for zinc is 29.4 µg/L at 22 mg/L CaCO₃ hardness.
- Chromium. Some of the more definitive work on chromium toxicity has been performed at Hanford. Research on early life stages of Chinook salmon (Olson and Foster [1956] as cited in Becker 1990) indicated survival was effected at 80 µg/L chromium VI. Long term exposure (est. at 5 months post hatch) at 13 µg/L produced a reduction in growth. The chronic water quality standard is 11 µg/L for Cr VI and 110 µg/L for Cr III at 47 mg/L CaCO₃ hardness. Recent studies in response to concerns over infiltration of ground water at Hanford have essentially duplicated these earlier results. In these more recent tests, there was no mortality observed at concentrations as high as 100 µg/L Cr VI (Patton et al. 2001).
- Arsenic. Water quality data on arsenic are shown in Table 6 for As V. Toxicity and chemistry of arsenic has been reviewed by Eisler (1988) and Neff (1997). Arsenate (V) is the dominant form in both freshwater and marine environments, however, arsenite (III), which is more toxic than arsenate, may also be formed along with organic complexes.

Overall, existing water quality standards appear to be protective of all aquatic life and no new research was uncovered that would suggest lowering those criteria.

Avoidance

Installation of treated wood structures and the resulting release of metals may result in avoidance reactions by fish. Laboratory and field studies have shown that rainbow trout and atlantic salmon can detect and will avoid zinc, copper, and chromium (Anestis and Neufield (1986), Sprague et al. 1965, Sprague 1964, 1968). For recently completed treated wood structures, the leaching of these metals into the water could result in avoidance behavior by salmonids. The possible impacts associated with avoidance behavior are varied and site specific. Fish avoiding a structure may become more subject to predation. Displaced fish may have to spend more time and energy procuring food if a structure was installed in a productive nursery area. On the other hand, fish will avoid exposure to contaminants and if migrating downriver, fish may reduce their transit time to sea if entrained in faster currents. There have been no specific studies, either laboratory or field studies, that have specifically demonstrated avoidance impacts as a result of used of treated wood in aquatic environments. The potential for impacts should be assessed on a site-specific basis for migrating salmonids.

Sediment Standards

A lot of research has been conducted over the past fifteen years attempting to better quantify sediment impacts of trace metals and risk to aquatic biota. Standards are promulgated in the Washington Administrative Code (WAC-173-204) for marine sediments (Table 7). There are no promulgated standards in Washington for freshwater sediments. These standards are based on a bulk dry weight basis.

Table 7. Washington State standards for marine sediments

Metal	Copper	Chromium	Arsenic	Zinc
mg/kg dry wt.	390	260	57	410

The criteria listed in Table 8 and described below are taken from Long et al. (1995) and are identified as National Oceanic and Atmospheric Administration (NOAA) values. This designation does not confirm endorsement by NOAA and is the authors convention. Other entities proposing benchmarks include the Florida Department of Environmental Protection (FDEP) and Region IV of the Environmental Protection Agency (Jones et al. 1997).

Table 8. Sediment benchmarks for trace metals (mg/kg dry wt.)

	NOAA ^a		FDEP ^b	
	ER-L	ER-M	TEL ^c	PEL
Copper	34	270	18.7	108
Chromium	81	370	52.3	160
Arsenic	8.2	70	7.24	41.6
Zinc	150	410	124	271

^a National Oceanic and Atmospheric Administration, as identified by Jones et al. (1997), however these are not authorized NOAA standards (Table 1, Jones et al. 1997)

^b Florida Department of Environmental Protection (Table 1, Jones et al. 1997)

^c Environmental Protection Agency, Region IV (Table 5, Jones et al. 1997)

The NOAA criteria were developed for marine and estuarine sediment locations and are based on data compiled by Long et al. (1993). Klapow and Lewis (1979) demonstrated that there was no significant difference in the median response from freshwater and marine organisms during acute toxicity tests using As, Cd, Cr, Cu, Pb, Hg, Ni, Ag, and Zn. Consequently, the NOAA criteria could be used for freshwater sediments as well. NOAA's criteria are split into two groupings, Environmental Response-Low (ER-L) and Environmental Response-Median (ER-M). The ER-L values represent the lower 10th percentile of observed biological effects and the ER-M value represents the median level for which there was a biological response. The "NOAA" values were developed to aid in the identification of sediments that have the potential to cause adverse biological effects and were not intended for regulatory decisions.

The FDEP sediment guidelines included a threshold effect level and a probable effect level. The TEL is the geometric mean of the 15th percentile in the no effects database and the 50th percentile of the data set effects and it represents the upper limit of the range of sediment contaminant concentrations dominated by no effects data. The PEL is the geometric mean of the 50th percentile of the data set for effects and the 85th percentile of the no effects data set. The PEL represents the lower limit of the range of contaminant concentrations associated with adverse effects.

Metals have a strong propensity to adsorb to particulate material in aquatic environments. Adsorption may be both organic material (dissolved complexes or solid phase particulate associations) and inorganic fractions (fines or silts and clay fractions). Consequently, sediments with a large component of fines have a greater capacity to adsorb metals. In this regard, divalent metals (copper and zinc) have a greater capacity to bind to sediments by cation exchange mechanisms than do arsenic and chromium. Another mechanism of metal binding and potential bioavailability involves binding to sulfides.

Simultaneously-Extracted Metals/Acid Volatile Sulfides (SEM/AVS)

One approach to assessing the risk posed to aquatic biota by trace metals involves estimating bioavailability of metals in the sediment (Long et al. 1998a, Lee et al 2000a, 2000b). Dissolved divalent metals in sediment pore water may be estimated based on thermodynamic data and the amount of acid volatile sulfides in the sediment. Copper and zinc are the two metals associated with treated wood that would be influenced by AVS. Essentially, each divalent trace metal has a potential to bind with sulfides present in sediment. The ability of sulfides to bind metals is related to the solubility product (K_{sp}) of each metal. Solubility products for metal sulfide complexes (as recorded in Dean (1992), Weast and Astle 1982) indicate the following relationship: mercury ($K_{sp} = 10^{-49}$ to 10^{-53}) < copper ($K_{sp} = 10^{-36}$ to 10^{-45}) < cadmium ($K_{sp} = 10^{-27}$ to 10^{-29}) = lead ($K_{sp} = 10^{-28}$) < nickel ($K_{sp} = 10^{-19}$ to 10^{-26}) = zinc ($K_{sp} = 10^{-22}$ to 10^{-24}) < iron ($K_{sp} = 10^{-18}$ to 10^{-19}). The smaller the K_{sp} value, the greater affinity (and proportionally, the amount) of metal that is tied up by available sulfides. The order presented, therefore, shows the order in which metals are sequestered by sulfides in sediments. As long as sulfides are not limiting, copper will complex with sulfide before Zn. Once all the sulfides have been complexed, metals with the lower K_{sp} values will appear in the sediment pore water in their reverse order portrayed

above. With respect to treated wood and in particular ACZA treated wood, copper that deposits into sediments would preferentially complex before zinc, and as available sulfides are complexed, zinc would dissolve into the pore water before copper.

SEM/AVS has received considerable attention over the past decade. The value of the method has been questioned, however, theoretically, it is sound. When applied, however, problems can arise when sediments are being assessed that contained toxic chemicals in addition to divalent trace metals (Long et al. 1998b). Another factor is that the high dissolved solid concentrations associated with estuarine and marine sediments may also influence SEM/AVS assessments. Studies have shown that ingestion of sediment may have a more significant role in accumulation of metals than geochemical partitioning between pore water and sediment adsorbed metals (Lee et al. 2000c). SEM/AVS may have application where metals are being introduced into the sediments of relatively pristine environments, but the approach needs more development before it has practical application in situations where treated wood projects are planned and sediments are already influenced by multiple anthropogenic contaminants.

Key Studies

Most of the critical studies focus of field studies involving the installation of treated wood in aquatic habitats. Most of this work involves CCA Type C treated southern yellow pine from studies conducted on the east coast. Relevant studies on bridges and boardwalks were included.

Marine CCA Treated Wood Studies - Atlantic Coast

A substantial body of research on CCA treated wood has been performed along the Atlantic coast under the direction of Rutgers University scientists J. S. Weis and P. Weis. Initial studies were laboratory investigations that assessed the toxic potential of CCA treated wood leachates in static exposure systems (Weis and Weis 1992, 1996; Weis et al. 1991, 1992). The initial laboratory studies involved the testing of leachates generated in closed static systems (Weis and Weis 1996). These test demonstrated the toxicity of leachates and also demonstrated that weathered treated wood produced less toxic leachates than new treated wood. Toxicity was most strongly link to copper in the leachates. Subsequent work focused on epibiota that could tolerate the exposure to metals used to preserve CCA Type C treated wood. Field studies demonstrated that green algae growing on CCA Type C treated wood docks would accumulate copper, chromium and arsenic above levels in algae growing on rocks. The levels of metals accumulated by epibiota growing on treated wood decreased with the age of the structure. Snails fed algae that had been growing on CCA treated wood docks displayed the same symptoms as snails exposed to leachates and died. Similarly, carnivorous snails fed oyster tissue collected from a CCA wood dock showed reduced growth.

Communities that populated new CCA treated wood panels were less diverse and had lower species richness. Accumulation of metals was also higher than the control treatments. Treated wood that was leached for 2 months sustained communities that were similar to the control

treatments (diversity, richness, biomass), but had elevated concentrations of metals. In concluding their review, Weis and Weis (1996) stated that the extent and severity of impacts resulting from CCA treated wood depended on the amount of wood installed, its age, and the amount of dilution or flushing in the aquatic system. The authors point out that environmental impacts could be reduced by pre-leaching CCA treated wood before installation.

The laboratory studies were followed with field investigations that better defined the risk associated with installation of treated wood structures in marine coastal environments (Weis et al. 1998).

Five CCA-Type C treated wood bulkheads were evaluated. Metal concentrations (copper, chromium, and arsenic) in sediment, marine polychaete worms (copper and chromium), benthic invertebrate communities (diversity, abundance, and biomass), and basic sediment, characterization (total organic carbon and percentage fines) were determined at each site. A reference control site was evaluated with the particular treated wood installation at each site. All five sites were located in residential areas with no industry nearby. The basic sampling design involved sampling at the bulkhead and at distances of 1, 3, and 10 m from the structure. Reference locations were bulkheads constructed of concrete (site 5), aluminum (sites 1 & 3), or simply open shoreline (sites 2 & 4). The age of the treated wood bulkheads ranged from 1 to 8 years. The amount of CCA Type C treated wood used in each bulkhead was not specified.

Sediment Metal Concentrations

Sediment concentrations of copper and arsenic were generally elevated at “0” and 1 m from the treated wood bulkheads. At 3 and 10 m sample transects, metal concentrations were not distinguishable from background. Chromium sediment concentrations were slightly elevated at the treated wood bulkheads in two structures, both of which were ≤ 2 years old. Evaluation of metal concentrations was confounded by differences in sediment TOC levels and percentage fines. Generally, both of these sediment parameters tended to increase at greater distances from the bulkhead. The inclusion of reference locations at each treated wood bulkhead structure was an asset to the design, but its overall value was diminished by confounding influence of variability in sediment TOC and percentage fines.

Polychaete Metal Concentrations

Elevated copper and arsenic were observed in polychaete worms at the treated wood structure and 1 m away at site #1 (one-year old site). Polychaete worms did not indicate any elevation of copper or chromium relative to the treated wood bulkheads at sites 2 through 4. No values for arsenic were reported at treated wood bulkhead sites 2 through 4. It is difficult to evaluate the elevated copper and arsenic levels because they can not be related to an adverse effect.

Benthic Community Evaluation

Community effects at the treated wood bulkhead sites can be demonstrated as gradients moving away from the treated wood bulkhead structure towards open water. Biotic community impacts

were evident at all five sites, however, demonstrable effects were limited to the treated wood bulkhead site (“0 m”; sites 2 and 4) or at both the site (“0 m”) and at 1 m (sites 1,3 and 5). These community effects may also be related to changes in sediment TOC and percentage fines. Generally, significant changes (about a factor of 10 or greater) in TOC and percentage fines were observed along the treated wood bulkhead transects at sites 1, 2, and 3.

Another approach to evaluating the effects of the treated wood structures was to compare biotic response to the reference locations, particularly those that had either a concrete or aluminum bulkhead installed. However, these comparisons are somewhat confounded by variability in sediment TOC and % fines and the relationship as not as clear-cut as was the case with the gradient approach.

Summary

Collectively, Weis et al. (1998) demonstrated elevations of sediment metal concentrations at and adjacent to CCA treated wood bulkheads. In association with the sediment metal observations, benthic communities were also impaired as indicated by abundance and diversity estimates. The authors note that for the older bulkheads, storm events could have transported contaminated sediments away from the bulkheads since they were first installed. This may explain the general tendency for impacts at site 2 and site 5 (both 6 to 8 years old) to appear less severe than effects at the newer sites, in particular, site no. 1 (one-year old).

Another observation is that some sites are less turbulent than others. Site 5, a 7- to 8-year old site at the mouth of the Patuxant River, Maryland, has much more “hydraulic” energy than poorly flushed tidal sites 2, 3, and 4.

In either case, spatially, demonstrable effects were limited to benthic communities at and out to 1 m from the treated wood bulkheads. These effects were likely attributable to metal contaminants in the sediments and interactions with fines and organic carbon.

South Carolina DNR Dock Studies

The South Carolina Department of Natural resources conducted several studies addressing potential impacts of CCA Type C treated wood in coastal environments in South Carolina (Van Dolah et al. 1992, Wendt et al. 1996). Initially, Van Dolah et al. 1992 assessed oyster populations (*Crassostrea virginica*) around marinas and concluded that there were no adverse biological effects in oyster populations attributable to proximity to marinas, however, spat settlement was likely related to poor tidal flushing. A subsequent expanded field study was conducted at ten high-density dock sites (each with a corresponding reference location) located within the Charleston Harbor estuary and associated tidal creeks. Reference sample sites (without docks) were selected to match salinity, tidal flux, and basic geomorphometry with their corresponding dock sites. Sampling “zones” at each treated wood site were established at <1 m from the dock, > 10 m from the dock, and at the reference station.

The basic design of the study was to look at metals (copper, chromium, arsenic) and PAH in sediments and oysters at both the dock sites and the reference sites (Phase I). Biological effects on resident oysters were also assessed by evaluating shell thickness and physiological condition (condition index). Additionally, solid phased sediment toxicity was assessed with Microtox assays. Sediment pore water toxicity was assessed with 24-hour toxicity tests using the rotifer *Branchionus plicatilis*. In addition to assessing resident oyster populations, laboratory reared oysters and estuarine fish were placed in pens near the dock structures and at reference locations to assess acute (96-hour for fish) and chronic (6-week exposure for oyster) toxicity of metals and PAH. These later “phase II” tests were performed at CCA Type C treated wood docks that were 4 to 12 months old and focused on assessing potential acute effects of leachates from CCA treated wood structures.

Sediment Contamination

The study characterized the fine grain component of sediments, but did not conduct analyses for TOC. Sediment metal concentrations were normalized to aluminum sediment concentrations to control for the propensity of metal contaminants to associate with silt and clay sediment fractions. Mean concentrations of copper, chromium and arsenic were slightly higher at locations near (< 1 m) docks, but the tendency was not statistically significant and was influenced by one or two outlier values. When normalized to aluminum levels, only one site showed elevated copper. The maximum un-normalized copper concentration was 401 µg/g sediment dry wt. Otherwise, there was no difference between sediment metal concentrations collected from sample near the dock, distant from the dock, and the reference locations.

Oyster Metal Concentrations

Resident oysters were also sampled and analyzed for metals. Concentrations of copper were significantly higher in oysters collected within 1 m of docks (226 [± 46 s.e.] µg/g dry wt.) when compared to oysters collected > 10 m from docks (134 [± 38 s.e.] µg/g dry wt.) and the reference locations (115 [± 20 s.e.] µg/g dry wt.). Chromium was at or below detection at the three sampling locations and mean arsenic concentrations ranged from 7.6 to 8.4 µg/g dry wt. There was no systematic decrease in chromium or arsenic levels with distance from the docks.

Biological Effects: Summary

There were no significant differences in oyster condition indices between the dock zones and the reference locations. Mean indices ranged from 7.88 at the reference sites to 8.01 at the dock sites. There were also no significant differences in shell thickness between sites. However, there was a significant correlation with increasing arsenic concentrations in oysters with decreasing shell thickness that was not apparent with copper concentrations (or chromium concentrations that were below detection in oyster tissue). The relationship was not attributable to sampling zones and may reflect natural deposits of arsenic associated with phosphate minerals in the area.

Solid phase Microtox tests did not indicate any difference in bacterial light production among the three zones that were sampled. There were significant negative correlations with Mircotox

results for specific docks, however, with dry weight sediment concentrations of copper, with arsenic in sediments, and also with dock density (number of docks per km shoreline). The authors note that sediment concentrations of copper, chromium and arsenic did not correlate positively or negatively with dock density.

The rotifer bioassays did not indicate any toxicity associated with the pore water extractions from any of the sampling sites. Associated 24-hr LC₅₀ concentrations for copper and chromium in rotifers are 120 and 115 µg/L, respectively.

Ninety-six hour field toxicity tests with mud snails (*Ilyanassa obsoleta*), mud minnow (*Fundulus heteroclitus*), juvenile red drum (*Sciaenops ocellatus*), and juvenile shrimp (*Penaeus setiferus*) were conducted at dock sites and reference locations. No differences in percentage survival were observed for any of these four species between the dock locations and reference locations. Oysters were also tested after six weeks field exposure. After six weeks, there were no significant differences between dock sites and reference locations for four test parameters: survival, mean shell width, mean shell height, and mean total wet weight. There was no difference in accumulated copper or arsenic in soft tissue of the oysters for either reference or dock locations (chromium was not detected).

Summary

This study suggests that measurable ecological effects of treated wood installations in estuarine environments with moderate tidal fluctuations (1.5 to 2.0 m) have minimal effect on acute toxicity and growth or survival of oysters. Copper accumulated in sediment and resident oysters in samples near docks (<1 m) to levels above those observed at reference locations and sampling sites >10 m from the docks. The elevated copper concentrations in resident oysters did not have an adverse impact on oyster growth or condition index.

While some data was presented about the number of docks present, the actual amount of treated wood was not quantified. For Phase I, some of the docks were likely treated with creosote as PAH were part of the analytical suite of toxicants.

New York Mussel Study

Filter feeding bivalve mollusks have the propensity to accumulate high concentrations of metals because of their feeding behavior. Blue mussels (*Mytilus edulis*) were exposed to CCA Type C treated wood (and as a control, untreated wood) in a flow through seawater system and in field deployed pens (Adler-Ivanbrook and Breslin 1999). Flows in the laboratory experiments were designed to simulate tidal flows and dilution. Flow rates of 13 L/min were used to leach the treated wood and expose the mussels. Two sets of exposures were conducted, one for 9 months, and the other for 3 months. The ratio of the treated wood surface area to flow was 10 cm²:1 L in the first 9-month experiment and 45:1 in the second 3-month exposure. Samples were collected up to five times through the duration of the exposures. Some facility problems that resulted in mortality of both control and treatment mussels impacted the study, but because impacts of these

problems were uniformly observed in all treatments, the authors were able to arrive at some sound conclusions regarding exposure to leached copper, chromium and arsenic. Conclusions drawn from these studies suggest the following.

There were no biological effects in the mussels resulting from exposure to leached metals. Endpoints included length, dry weight, condition index and mortality. Moreover, there were no significant differences in the accumulation of metals between the exposed groups and non-treated wood controls that could be attributed to treated wood. The lack of metal accumulation indicates that the flow through regime provided sufficient dilution of leached metal contaminants that tissue levels did not increase over levels sustained at exposure to natural background concentrations. Leaching of metals from CCA treated wood dropped significantly after initial immersion in seawater.

In summary, these field and laboratory experiments demonstrated no adverse impact to mussels in systems that represented the degree of dilution that would be associated with a treated wood structure.

Marine Bridge Studies in Florida

In 1997, the US Forest Service initiated a study of a large bridge constructed with CCA Type C treated wood in Florida with Aquatic Environmental Sciences as the lead contractor (Brooks 2000a). The 282-ft Horseshoe Bayou Bridge was constructed in March 1998 across Choctawhatchee Bay in Sandestin, midway between Pensacola and Panama City, FL. It consisted of 87 southern yellow pine pilings treated to a retention of 2.5 pcf CCA Type C preservative. The over-water support beams and decking were treated to 0.4 pcf CCA Type C. The evaluation of the bridge was initiated on March 22, 1998 when construction was nearing completion. Choctawhatchee Bay is a marine environment with salinities of 25 ppt.

The study design included a control site 175 ft distant and sampling sites located immediately beneath the bridge and seaward at 1.5, 3, 6, 10 20 and 33 ft downstream of the structure.

Water Column Impacts

Water samples were collected at 8 transect locations and analyzed for dissolve copper, chromium and arsenic.

- Copper. Concentrations of dissolved copper at and downstream of the bridge ranged from 1.6 to 1.9 µg/L compared to the upstream 175-ft reference concentration of 2.0 (± 0.4 95% C.I.) µg/L. For comparison, the marine chronic water quality standard for dissolved copper is 2.5 µg/L.
- Chromium. Concentrations of dissolved chromium (VI) at and downstream of the bridge ranged from 1.7 to 2.1 µg/L compared to the

upstream concentration of 1.8 (\pm 0.25 95% C.I.) $\mu\text{g/L}$. The marine chronic water quality standard for chromium (VI) is 50 $\mu\text{g/L}$.

- Arsenic. Concentrations of dissolved arsenic at and downstream of the bridge ranged from 6.2 (\pm 0.43 95% C.I.) to 7.4 $\mu\text{g/L}$ compared to the upstream concentration of 8.3 (\pm 2.1 95% C.I.) $\mu\text{g/L}$. For comparison, the marine chronic water quality standard for dissolved arsenic is 36 $\mu\text{g/L}$.

None of the three metals associated with CCA treated wood exceed marine water quality standards in water samples collect at and “downstream” of the bridge.

Water Column Toxicity Tests

Water was collected at low slack tide 16 cm from the piling structure, filtered at 0.45 microns, and used for exposing a marine amphipod (*Menidia merylina*) for 96 hours. Survival in laboratory controls, the upstream control location, and at 1.5, 6 and 33 ft downstream ranged from 87.5% (1.5 ft downstream) to 92 % with no significant difference between tests.

Sediment Impacts

Sediment samples were collected at 8 transect locations and analyzed for copper, chromium and arsenic. The authors noted that there were accumulations of treated wood sawdust from holes that were drilled during bridge construction. Metal concentrations were highly variable at and below the bridge, but the three upstream controls yielded consistent results for all three metals.

- Copper. The mean sediment copper concentration was 11.9 (\pm 13 [95% C.I.]) mg/kg dry wt. beneath the bridge; the maximum value (of three samples) at this location was 25.1 mg/kg. There was a general decreased in concentrations downstream of the bridge from 7.95 mg/kg at 1.5 ft downstream to 1.8 mg/kg 33 ft downstream. The mean background sample (175 ft upstream) was 2.4 (\pm 0.24 [95% C.I.]) mg/kg of copper.
- Chromium. The mean sediment chromium concentration was 23.6 (\pm 30 [95% C.I.]) mg/kg dry wt. beneath the bridge; the maximum sediment value (of three samples) was 54.3 mg/kg. There was a generalized decreased in mean concentrations downstream of the bridge from 17.2 mg/kg at 1.5 ft downstream to 3.2 mg/kg 33 ft downstream. The mean background sample (175 ft upstream) was 4.1 (\pm 0.82 [95% C.I.]) mg/kg of chromium.
- Arsenic. Concentrations of arsenic were much more variable than copper and chromium. The mean sediment arsenic concentration was 9.8 (\pm 15 [95% C.I.]) mg/kg dry wt. beneath the bridge. The maximum concentration was 31 mg/kg, and was observed 3.0 ft downstream. Mean sediment concentrations at 10 ft to 33 ft downstream ranged from 0.55 to

0.85 mg/kg arsenic. The mean background sample (175 ft upstream) was 0.8 (\pm 0.1 [95% C.I.]) mg/kg of arsenic.

For all three metals, sediment impacts based on sediment concentration appeared to be limited to 6 ft, and no more than 10 ft downstream of the bridge. Washington State marine sediment standards are 390 mg/kg for copper, 260 mg/kg for chromium, and 57 mg/kg for arsenic. The maximum measured concentrations of metals did not exceed existing WAC guidelines. Measured concentrations of chromium and arsenic exceed the FDEP threshold sediment benchmark levels of 52.3 and 7.24 mg/kg, respectively (see Table 7).

Biological Effects: Benthic Invertebrate Population Assessment

Biological effects at both bridges were assessed with analysis of benthic invertebrate populations. Benthic invertebrate samples were collected at the sediment sampling locations and the different species were identified and counted to provide these calculations and support factor analysis. The data was quantified in terms of overall abundance and in two indices: 1) Shannon's Index for diversity – richness, and 2) Pielou's Index for Diversity - evenness. Calculations of Shannon's index range from 0 to 3 with values ≥ 2 indicative of a healthy or un-impacted benthic ecosystem. Calculations of Pielou's Index range from 0.0 to 1.0. Values >0.5 are usually associated with a healthy or un-impacted benthic ecosystem.

Shannon's index values ranged from <0.6 to ~ 1.5 with no apparent relationship with orientation to the bridge or sediment concentrations. Pielou's index ranged from ~ 0.25 to ~ 0.5 with no specific relationship to the bridge or sediment. Both indices are generally indicative of reduced diversity, however there was no apparent relationship between these diversity indices and sediment metal concentrations or proximity with the bridge.

Freshwater Bridge Studies – Florida

In 1997, the US Forest Service initiated a study of a large foot bridge constructed with CCA Type C treated wood in Florida (Brooks 2000a). The 100-ft Fountains Bridge was constructed in 1997 across a freshwater marsh in Sandestin, FL, midway between Pensacola and Panama City, FL. The pedestrian bridge appears to be supported by a total of 16 pilings. The evaluation of the bridge was initiated on March 22, 1998 when the bridge was about 2 years old. The marsh is basically standing water with a total hardness of 59 mg/L CaCO₃ equivalents, alkalinity of 17.1 mg/L CaCO₃, and a pH of 6.1 to 6.4.

The study design included a reference station 100 ft “downstream” and sampling sites located immediately beneath the bridge and seaward at 1.5, 3, 6, 10, 20 and 33 ft downstream of the structure.

Water Column Impacts

Water samples were collected at 8 transect locations and analyzed for dissolved copper, chromium and arsenic.

- **Copper.** Concentrations of dissolved copper at and downstream of the bridge ranged from 1.4 to 2.6 µg/L compared to the 100-ft reference station concentration of 2.3 µg/L. The freshwater chronic water quality standard for dissolved copper at 59 mg/L hardness is 6.9 µg/L.
- **Chromium.** Concentrations of dissolved chromium (reported as “total”) at and downstream of the bridge ranged from 0.44 to 1.6 µg/L compared to the upstream concentration of 2.1 µg/L. Interestingly, concentrations of chromium increased with distance from the bridge. The freshwater chronic water quality standard for chromium (VI) is 11 µg/L.
- **Arsenic.** Concentrations of dissolved arsenic at and downstream of the bridge ranged from 5.4 to 7.5 µg/L compared to the upstream concentration of 6.6 µg/L. The freshwater chronic water quality standard for arsenic is 190 µg/L.

All measured concentrations of metals were below chronic freshwater criteria.

Water Column Toxicity Tests

Water was collected from the vicinity of the bridge and used for toxicity testing on the freshwater crustacean (*Daphnia magna*) for 96-hour tests. Survival in laboratory controls was 90 %. Survival at the upstream control location was 85 %, and ranged from 77.5 % (6 ft downstream) to 87.5 % (33 ft) with no statistically significant difference between either the laboratory control and downstream bridge groups and the reference station (100 ft downstream) and the bridge treatments.

Sediment Impacts

Sediment samples were collected at 7 sampling locations (beneath the bridge and six location downstream) and a reference location 100 ft downstream of the bridge and analyzed for copper, chromium and arsenic.

- **Copper.** The mean sediment copper concentration was 2.1 (\pm 1.1 [95% C.I.]) mg/kg dry wt. beneath the bridge; the highest mean value was 2.2 (\pm 0.8 [95% C.I.]) mg/kg at 3 ft downstream. There was a decreased in copper concentrations downstream of the bridge to a low mean concentration of 0.7 (\pm 0.2 [95% C.I.]) mg/kg dry wt. at 20 ft downstream. The background samples (100 ft downstream) was 0.63 (\pm 0.46 [95% C.I.]) mg/kg dry wt.

- Chromium. The mean maximum sediment chromium concentration was 3.2 (\pm 1.2 95% C.I.) mg/kg dry wt. beneath the bridge. There was a generalized decreased in concentrations downstream of the bridge to 1.1 (\pm 0.6 [95% C.I.]) mg/kg dry wt. 33 ft downstream. The mean background sample (100 ft downstream) was 1.0 (\pm 0.5 [95% C.I.]) mg/kg dry wt. of chromium.
- Arsenic. The mean sediment arsenic concentration was 1.5 (\pm 0.7 [95% C.I.]) mg/kg dry wt. beneath the bridge. The maximum concentration was 4.3 (\pm 5.1 [95% C.I.]) mg/kg dry wt., measured 1.5 ft downstream of the bridge. Mean sediment concentrations dropped to 0.45 (\pm 0.08 [95% C.I.]) mg/kg dry wt. at 10 ft downstream and then ranged from 0.40 to 0.63 mg/kg dry wt. at the remaining downstream sampling locations. The mean background sample (100 ft downstream) was 0.57 (\pm 0.17 [95% C.I.]) mg/kg dry wt. of arsenic.

For all three metals, increased sediment concentrations appeared to be limited to 6 ft, and no more than 10 ft downstream of the bridge. The maximum measured concentrations of each trace metals fell below the threshold effects level (TEL- Region IV EPA) for copper (3.0 mg/kg – TEL = 18.7 mg/kg), chromium (3.7 mg/kg – TEL = 36 mg/kg) and arsenic (7.5 mg/kg, TEL = 11 mg/kg), respectively (Jones et al. 1997). The values summarized by Jones et al. 1997 are benchmarks and are provided as an indication of potential “threshold” impact as well as an upper bound for impacts.

Oregon Boardwalk Study

The U.S. Forest Service conducted assessments of several varieties of treated wood in a wetland boardwalk including CCA Type C treated western hemlock (11.7 kg/m³) and ACZA treated Douglas fir (7.04 kg/m³). The study area was a wetland with boardwalks and viewing platforms constructed of different types of treated wood. The boardwalks and viewing platforms were constructed on solid ground and over freshwater marshes in Oregon (ph < 6.8, very low alkalinity (<23 mg/L CaCO₃)). CCA Type C and ACZA were used for some of the installations. Data on leaching of wood preservatives and subsequent accumulated in soil and sediment were collected and assessed (Lebow et al. 2000). Ecological effects were also evaluated at each structure over the course of a year (Brooks 2000b).

CCA Type C Treated Wood

For CCA Type C treated wood, field leaching rates were estimated as a function of rainfall, and surface area for five deck boards associated with a foot bridge constructed across a marsh channel. The deck boards were aberrant in two ways. The total retention of fixative for these deck boards (2.99 kg/m³) was less than the target design retention of 6.4 kg/m³. Consequently, the associated leaching rates may not represent leaching rates of treated wood that is preserved to BMP standards, even though the intent was to use BMP treated wood (Table 9). Second, rates of

arsenic leaching were greater than copper and chromium (Lebow et al. 2000). This observation, which is contrary to the expected leaching of metals, may be related to the sub-standard retention level of fixative.

Table 9. Release rates ($\mu\text{g}/\text{cm}^2/\text{in. rain}$) CCA Type C treated western hemlock.

Time	Rainfall	Arsenic (As_2O_5)	Copper (CuO)	Chromium (CrO_3)
2 months	4.3 in.	1.8	0.9	0.3
5.5 months	26.3 in.	0.75	0.3	0.2
11 months	108 in.	0.3	0.1	0.1

All three CCA leachable metals accumulated to elevated levels above background levels in sediment collected at the edge of the structure and at distances away from the boardwalks. Sediment samples were collected at two depths, 0 to 2.5 cm, and 2.5 cm to 10 cm. Sample times were at 0.5, 2, 5.5, and 11 months post installation and were compared to pre-installation levels and to a distant control location.

Arsenic accumulation over the 11-month duration of the study varied both temporarily and spatially. Baseline arsenic levels ranged from 2 to 4 mg/kg dry weight in superficial sediments (0 to 2.5 cm depth). Geometric mean concentrations of arsenic increased to levels as high as 41 (maximum = 130) mg/kg beneath the boardwalk at 2 months. At 11 months, concentrations of elevated arsenic (geometric mean = 13 mg/kg) were observed up to 3 m (10 ft) from the structure.

Copper accumulation over the 11-month duration of the study varied both temporarily and spatially. Baseline copper levels ranged from 19 to 24 mg/kg dry weight in superficial sediments (0 to 2.5 cm depth). Geometric mean concentrations of copper increased to levels as high as 112 (maximum = 219) mg/kg beneath the boardwalk at 5.5 months. At 11 months, concentrations of elevated copper (geometric mean = 44 mg/kg) were observed up to 0.6 m (2 ft) from the structure.

Chromium accumulation over the 11-month duration of the study varied both temporarily and spatially. Baseline chromium levels ranged from 9 to 14 mg/kg dry weight in superficial sediments (0 to 2.5 cm depth). Geometric mean concentrations of chromium increased to levels as high as 33 (maximum = 104) mg/kg beneath the boardwalk at 2 months. At 11 months, concentrations of elevated chromium (geometric mean = 21 mg/kg) were observed beneath the structure and with no consistent indication of migration away from the structure.

Brooks (2000b) evaluated the distribution of benthic invertebrates both as a function of distance and contaminant loading in the sediments below and adjacent to the CCA Type C boardwalk structure. Essentially, none of the population indices (abundance, Shannon's Index, Pielou's Index) indicated an adverse relationship that could be related to the boardwalk structure. Rather,

where possible differences were observed, they were not systematically associated with contaminant gradients of spatial relationship with the boardwalk.

ACZA Treated Wood

Brooks (2000b) evaluated the distribution of benthic invertebrates both as a function of distance and contaminant loading in the sediments below and adjacent to the footbridge. Copper had the highest initial release rates, but arsenic release rates were similar to copper release rates in subsequent sampling periods (Table 10). Dominant species abundance was significantly increased downstream of the bridge, however, there was no correlation with sediment level contaminants for copper or arsenic. Essentially, none of the population indices (abundance, Shannon's Index, Pielou's Index) indicated an adverse relationship that could be related to the boardwalk structure. Rather, where possible differences were observed, they were not systematically associated with contaminant gradients attributed to the bridge. These effects may likely be random events.

Table 10. Release rates ($\mu\text{g}/\text{cm}^2/\text{in. rain}$) ACZA treated western hemlock.

Time	Rainfall	Arsenic (As_2O_5)	Copper (CuO)	Zinc (ZnO)
2.5 months	10.7 in.	1.8	5.2	3.3
6 months	32.7 in.	2.2	2.0	0.9
11.5 months	114.7 in.	1.1	1.0	0.6

All three ACZA leach-able metals accumulated to elevated levels above background levels in sediment collected at the edge of the structure and at distances away from the boardwalks. Sediment samples were collected at two depths, 0 to 2.5 cm, and 2.5 cm to 10 cm. Sample times were at 0.5, 2, 5.5, and 11 months post installation and were compared to pre-installation levels and to a distant control location.

Arsenic levels increased temporarily over the 11.5-month duration of the study. Baseline arsenic levels ranged from 1 to 2 mg/kg dry weight in superficial sediments (0 to 2.5 cm depth). Geometric mean concentrations of arsenic increased to levels as high as 13 (maximum = 46) mg/kg beneath the boardwalk at 11.5 months. At 11.5 months, concentrations of elevated arsenic were observed beneath the structure with non-statistically significant increases observed at 30 cm (1ft) from the structure.

Copper accumulations increased temporarily and spatially over the 11.5-month duration of the study. Baseline copper levels ranged from 18 to 21 mg/kg dry weight in superficial sediments (0 to 2.5 cm depth). Geometric mean concentrations of copper increased to levels as high as 81 (maximum = 569) mg/kg beneath the boardwalk at 2.5 months. At 11.5 months, elevated geometric mean concentrations of elevated copper (44 mg/kg) were observed at 1.5 m (6 ft) from the structure. At 11.5 months, significant down gradient dispersion was limited to 0.3 m (1 ft) from the structure.

Zinc accumulations increased temporarily and spatially over the 11.5-month duration of the study. Baseline zinc levels ranged from 42 to 50 mg/kg dry weight in superficial sediments (0 to 2.5 cm depth). Geometric mean concentrations of zinc increased to levels as high as 213 (maximum was 1048) mg/kg beneath the boardwalk at 2.5 months. At 11.5 months, elevated geometric mean concentrations of elevated zinc (136 mg/kg) were observed beneath the structure. At 11.5 months, significant down gradient dispersion was observed at 1.5 m (5 ft) from the structure (geometric mean of 75 mg/kg). High accumulations of zinc in the sediments may also be related to the use of galvanized hardware on the boardwalk and viewing platform.

Brooks (2000b) evaluated the distribution of benthic invertebrates both as a function of distance and contaminant loading in sediments below and adjacent to the ACZA boardwalk structure. Essentially, none of the population indices (abundance, Shannon's Index, Pielou's Index) indicated an adverse relationship that could be related to the boardwalk structure. Rather, where possible differences were observed, they were not systematically associated with contaminant gradients of spatial relationship with the boardwalk.

Assessment of Treated Wood

This review has identified some commonalities in the risks associated with the releases of contaminants from treated wood prepared with creosote or metals based preservatives. This study looked at marinas, private docks, bridges, observation platforms as well as specialized laboratory and field studies. No large-scale installations of treated wood, such as those present in large coastal cities were evaluated. Most researchers have avoided these areas because it is difficult to separate effects associated with the treated wood structure with other sources of PAH or metal contamination. Potential impacts can be modeled (e.g., Brooks 1996, NMFS 1998), however no example of a large-scale modeling and verification study of a large treated wood installation (>100 pilings) has been reported.

The overall conclusions of this assessment are:

- The propensity for trace metals or PAH to result in long-term water column impacts are much lower than their potential for impacts to sediment. Short-term acute toxic impacts are possible, but decreases in diffusion or leaching rates of contaminants over time reduces the risk of acute impacts in the water column.
- For the size of treated wood structures evaluated in this review, the spatial extent of impact is generally small and limited to areas in the immediate vicinity of the structure. Extra consideration needs to be given to large treated wood projects.
- The relative hazard of creosote treated wood is generally greater than the hazard associated with CCA Type C or ACZA treated wood in terms of temporal and spatial impact. Consideration needs to be given to site-specific conditions.

CCA Type C or ACZA treated wood is generally preferred to the use of creosote treated wood as a more environmentally friendly product.

This assessment focused heavily on field evaluations of treated wood risks to aquatic resources with possible application of risk to listed salmonids. Most of the field studies specifically addressing treated wood installations did not address salmonids as a targeted receptor. Temporal impacts and spatial impacts attributed to treated wood installation in aquatic habitats are summarized below. This discussion is followed by a short discussion of potential salmon impacts, data gaps research needs, potential methods to mitigate the toxicity of treated wood use, and key issues.

One generic issue is the applicability of current water and sediment standards. The whole arena of sediment standards is very much under development for both metals and PAH. The WAC has not issued standards for freshwater sediments for metals or PAH, and the standards for marine

sediments area based on amphipod toxicity tests and may not address other forms of exposure (food chain transport), ecological receptors, or endpoints. No part of this review identified a need to revise water quality standards for arsenic, chromium, copper, or zinc. A water quality standard for total PAH is desirable to address the complexities of this class of compounds. It is apparent that water quality standards for individual PAH would have little value for regulating this class of compounds to protect aquatic resources. Dissolved concentrations on the order of 0.4 to 1 µg/L total PAH were associated with developmental toxicity in cold water marine fish.

A second generic issue is the application of precautionary principle for the protection of listed species. A difficulty arises when treated wood installations occur in areas where other stressors (chemical or physical) have the potential to impact a valued resource specie or its habitat. In terms of cumulative impacts, it may not be possible to accurately assess what fraction of potential risk can be attributed to contaminants associated with a treated wood project. Those impacts, in turn, need to be evaluated with other impacts associated with the project amidst the possible backdrop of non-project related sources of stress to determine the overall significance of risk of a project. In pristine habitats, the potential impacts may be readily identified against a low back-ground of contaminants. In contrast, a high background of contaminants in an industrialized area may obscure any impact associated with a treated wood project.

Creosote Treated Wood

Adverse environmental effects associated with creosote treated wood are manifested in the accumulation of contaminants in sediment and direct impacts to biota that may colonize the treated wood structure. New installations of creosote treated wood usually result in the formation of an oil sheen consisting of some lower weight PAH. The lower weight PAH are more readily volatilized at the surface and are more quickly degraded than larger PAH. Generally, they are more acutely toxic and may also be assimilated more readily into the microlayer. The impact of these sheens is short term. Overtime, the distribution of PAH (between low- and high-molecular weight PAH shifts towards a larger percentage of high-molecular weight PAH in material released from treated wood (Goyette and Brooks 1998, 2000). It is the chronic release of PAH that ultimately impacts the sediment and associated benthic environment. Direct acute impacts to the water column from creosote treated wood installations are in relative terms, small and of short duration. Generally, they are due to the loss of excess preservative. Implementation of BMP processing has likely reduced the amount of excess creosote on modern treated wood products compared to earlier processes.

Temporal Extent of Impact of Creosote Treated Wood

The duration of diffusion of PAH from the retention zone of creosote treated wood is a long term process that may last the life of the product. PAH in creosote treated wood continue to diffuse from the product for decades. The degree of diffusion in BMP treated pilings, however, may not be as great as indicated by early studies involving older pilings and samples of treated wood. PAH accumulate in sediment where they will biodegrade over time. At some point in time, equilibrium may be achieved where the contribution of PAH from treated wood into aerobic

sediments is balanced or exceeded by the microbial and physical degradation of PAH in the sediment. PAH will persist for longer periods of time in anaerobic sediment.

Removal of creosote treated wood structures, particularly those emplaced in sediment over extended periods of time, may result in the temporary suspension of sediment contaminated with PAH. No information was found that specifically addresses this concern, however, most of the field data indicates that sediment accumulations of PAH are greatest at and immediately adjacent to the structure.

In-water creosote treated wood structures may be toxic to sessile organisms that intimately attach themselves to the structure. Tolerant species of sessile algae, barnacles and bivalve mollusks may attach themselves to pilings, but the organism is attached by metabolically inert structures (byssal thread, mineralized exoskeletons/shells). Other organisms are more intimately exposed on contact. Snails may be exposed while traveling over treated wood and by feeding on periphyton that can grow on treated wood. Organisms that lay eggs on open surfaces of treated wood may also have a more intimate exposure, e.g., spawning herring or snails. Pilings over 50 years old still contain sufficient amounts of creosote to kill herring embryos.

Marine organisms may colonize marine installations of treated wood. Colonization of pilings is a function of toxicity of wood preservatives in the structure and the tolerance of the colonizing organisms. The degree of colonization, in terms of number of organisms and diversity, may also be influenced by the ability of organisms to migrate to the pilings from adjacent habitat (i.e., recruitment). Colonization rates may be reduced in areas previously impacted by other sources of contamination of human activity (cumulative impacts).

Spatial Extent of Impact

Critical impacts resulting from the installation of creosote treated wood are dependent on the amount of treated wood installed, and the physical condition of the installation site. Key physical variables are the turn over of water (currents or tidal action) and the sediment characteristics. The key sediment characteristic for PAH is organic carbon content. These variables will have great impact on the fate of contaminants in the sediments. Few studies have been performed that specifically evaluate the impact of creosote treated wood structures. Creosote treated wood is not allowed in lakes in Washington and has limited use in rivers in inland Washington, and its use along the coast is limited primarily to estuarine and marine environments. Installations may range from a few pilings for small private docks to dense configurations for commercial and industrial purposes (e.g., Seattle water front).

Adverse impacts were noted in installations of 6-piling dolphins installed in the Sooke Basin (Goyette and Brooks 1998, 2000). Impacts were noted up to 7.5 m from the BMP creosote treated structures in terms of increases in sediment burdens of PAH. Biological indices of adverse impacts, however, were associated with toxicity tests and sampling within 2 m of the treated wood structures. However, the sampling of sediment away from the test dolphins demonstrated that PAH contamination was “patchy” and relatively mobile. The authors attribute

this to the migration and settling of PAH as micro-dispersions in the marine environment. Subsequent follow-on studies indicated that sediment concentrations of PAH had decreased when they had been expected to increase.

While most of the concern for creosote treated wood is focused on marine and estuarine applications, some studies have examined the use of treated wood in over-water structures such as bridges. A study was conducted along Pipe Creek in Indiana where a 2-year old bridge and a 17-year old bridge were evaluated (Brooks 2000a). Based on sediment burdens of PAH, the extent of influence of the bridge structure on PAH sediment levels extended to no more than 10 ft (3 m) downstream of the structure. In this section of the creek, flows were relatively slow (reported at ~1.0 cm/sec). Sediment toxicity tests with amphipods did not indicate any toxicity, however, due to technical problems, there was no supporting PAH chemistry of the sediments provided.

Spatially, the impact based on increases in sediment PAH was localized (less than 10 m (33 ft) for these small structures. No studies were found that evaluated the spatial extent of PAH attributed to large creosote wood structures (e.g., > 100 pilings).

CCA Type C and ACZA Treated Wood

Long term adverse environmental effects associated with CCA Type C and ACZA treated wood are manifested in the accumulation of contaminants in sediment and direct impacts to biota that may colonize a treated wood structure. Leaching rates of trace metals (primarily copper) from installations of CCA Type C and ACZA treated wood are greatest when the wood is first immersed in water. Comparatively, ACZA has initially higher rates of copper leaching when compared to CCA treated wood, however, leaching rates diminished more quickly in ACZA treated wood than in CCA treated wood. The impact to the water column is a short-term event (days to weeks) and contaminants that are leached are ultimately deposited into sediments. The differences between CCA Type C and ACZA treated wood are minor. More important, however, is that most environmental evaluations of metals based treated wood was conducted on CCA treated southern yellow pine. Additionally, most of that research was conducted in marine or estuarine environments.

Temporal Extent of Impact

Newly treated CCA Type C and ACZA wood contains an inventory of leachable metal that is released when treated wood is first installed into aquatic environments. This inventory of leachable metals is not immediately depleted in over water structures because removal is a function of precipitation events rather than constant emersion. The risk of immersed wood decreases over a short period of time (days to weeks) because the leaching of metal contaminants drops off. Over water structures may have numerous episodes of releases with precipitation events until that reservoir is depleted. In both cases, field studies indicated that any water column toxicity is minimized by dilution of the receiving waters and diminishes with the age of

the structure. Consequently, areas with low flow or low turnover and low pH have the greatest potential for adverse impacts.

Where metals (specifically copper) have accumulated in concentrations above background in filter feeding oysters, there was no measurable biological impact to those oysters. Others have reported impacts at and immediately adjacent to treated wood structures, and these localize impacts persist as long as the contaminant regime does not change. Metals will not in the long term degrade, they may however, become mineralized, chemically sequestered, or physically sequestered. The role of acid volatile sulfides in bioavailability of metals is unresolved at this point, but likely is a major factor.

Released metal contaminants will likely be incorporated into the sediment. This review of several field studies did not turn up one study where sediment impacts (as indicated by increases in metal concentration in the sediment) were supported by adverse biological response. Long-term accumulation of metals in sediment at the base of pilings emplaced in mud has not been reported. The risk associated with removal of pilings under this scenario is not well understood.

In-water CCA Type C and ACZA treated wood structures are likely toxic to aquatic organisms that may contact the surface. Tolerant species of sessile algae, barnacles and bivalve mollusks may attach themselves to pilings, but some organisms are attached by metabolically inert structures (byssal thread, mineralized exoskeletons/shells). Aquatic organisms that are tolerant of trace metals may colonize immersed treated wood structures. Weis and Weis (1996) report that several forms of aquatic biota accumulated metals above background, but what is not known is the degree of adverse impact on the organisms associated with the accumulation of metals. Contact toxicity has been demonstrated with snails fed algae that was grown on CCA treated wood.

From the studies reviewed, there was no indication that adverse impacts associated with leached metals from treated wood increase over time. The fact that leaching rates diminished over a short time frame (days to weeks) reduces the temporal extent of impact of metals based treated wood.

Spatial Extent of Impact

The potent for impacts on a spatial scale are determined by the amount of treated wood installed, and the physical condition of the installation site. Key physical variables are the turn over of water (river flow, currents or tidal action) and the sediment characteristics. The key sediment characteristics are percentage fines and organic carbon content. These variables will have great impact on the fate of contaminants in the sediments. The role of acid volatile sulfides in bioavailability is unresolved at this point, but is likely a key variable in metal toxicity. In rivers and streams, periodic flooding will displace and transport sediment. This process can reduce the potential for long-term accumulations of contaminants near treated wood structures, however, the sediment ultimately will be dispersed and deposited down stream, either behind dams or in estuaries.

Impacts of leached metals to sediments were localized at and immediately adjacent to small treated wood structures. Increases in sediment metal concentrations were limited to within 10 ft or less of small treated wood structures in marine and freshwater habitats. No adverse biological impacts from either sediment toxicity testing or *in situ* community changes were reported in the field studies reviewed. These observations were apparent in habitats that were prone to reduced water exchange and accumulation of sediment bound contaminants.

Impacts to Salmon

Going back to the life cycle description of salmon, the critical life stages are egg larval incubation in gravel and juvenile migration and residence in freshwater nursery areas and estuaries. Sediment conditions that facilitate the accumulation of PAH and trace metals (increased fines and organic content) are generally not found in riverine salmon spawning areas which are dominated by gravel and cobble and high inter-bed flow. Spawning habitats vary among species and may include areas under tidal influence (e.g., pink salmon spawn in gravel beaches at the confluence of streams and estuaries and sockeye salmon may spawn in both streams and lake side beaches (Burgner 1991, Heard 1991, Murphy et al. 1999). Nursery areas in both river and estuarine habitats may include areas that have sediments with high organic content and fines. Once juvenile salmon enter larger rivers or engage in an open-water marine life stage, the potential to be adversely impacted by treated wood contaminants is very low.

While leaching of contaminants has been a primary concern, other aspects of installation may also influence the potential exposure to salmon. Drilling and cutting of treated wood may introduce contaminated wood fragments into aquatic habitat. The use of galvanized hardware may introduce elevated levels of zinc into habitats. These concerns require dedication to construction practices that minimize the potential for exposure.

Creosote treated wood should not be installed in spawning areas of listed species of salmon because of its propensity for chronic releases and uncertainty regarding inter-gravel exposure near emplaced pilings or footings. If metals based treated wood is to be used in areas where salmon spawn, then installations should be scheduled to allow for sufficient weathering to occur to avoid exposure to eggs and larvae and minimize exposure to juvenile salmonids. The amount of metals based treated wood that is immersed in water should be minimized where possible if it is used. Creosote treated wood structures should not be constructed in low flow areas (i.e., small tributaries) where juvenile salmon are migrating, or where they may feed for extended periods of time (nursery areas, estuaries). Metals based treated wood structures can be used in these situations, but again mitigation should be considered to minimize exposure to sensitive life stages of listed fish and consideration given to cumulative impacts. Larger streams with large flows are not likely to create situations where treated wood contaminants will accumulate to detrimental levels in aquatic food webs. Where river flows decrease and sediments accumulate, the potential for exposure to released contaminants increases, but the field evaluations indicate that contaminants will not accumulate to deleterious concentrations at areas away from small treated wood structures. Each individual situation needs to be evaluated on its own merits in

terms of amount of treated wood installed, flow regime and other pertinent conditions at the site. The existing water and sediment quality of a site needs to be considered with respect to use of the area (e.g., wildlife recreational areas would require different considerations than the Seattle water front). Because creosote treated wood continuously releases contaminants, it poses more risk than metal-based treated wood.

Treated wood should be inspected before installation to ensure that there are not any superficial deposits of preservative material on the wood. Storage of treated wood at construction sites before installation should also be managed to minimize environmental releases of contaminants

The most probable route of exposure to leached or diffused contaminants from treated wood for salmon is through the consumption of contaminated prey. Hence, exposure is greatest for salmon when they are feeding in areas of sediment deposition (low flow areas) immediately adjacent to treated wood structures. Areas where there are a large number of creosote treated structures pose the greatest risk to listed salmon. It is uncertain if that risk is significant (the actual intake of PAH from treated wood has not been quantified) and that the resulting exposure in those situations results in appreciable harm to migrating salmon. Again, precautionary principle may be applied.

Last, this paper has focused most of its efforts towards impacts to salmonids. However, the preservation of wild salmonids populations is dependent on the preservation of suitable habitat and the biodiversity associated with healthy ecosystems. Wild populations of any species can not be protected or maintained in a natural state without having a functional ecosystem. To this end, protection of salmonids is dependent upon preservation of ecosystems and adequate habitat. To that end, evaluations of the use of treated wood should look at all components of the ecosystem to assess the ecological risk in time and space associated with its use.

Data Gaps

One approach to assessing impacts is the availability of sound water and sediment quality standards and benchmarks for assessing ecological impacts. Standards and benchmarks need to accurately identify concentrations that elicit biological response and impact. Past practices have at times invoked margins of safety when uncertainty about the significance and level of adverse effects was unknown and un-quantified. This review has identified several studies that may help define better benchmarks for assessing impacts.

Many of the reviewed studies suffered from lack of a more rigorous experimental design. This is not necessarily a deficiency of the underlying science. The limitations in experimental design may have significant grounding in the availability of resources in terms of funding and staffing. Some of the field studies that were reviewed here could have benefited from more frequent sampling, background (control site) characterization, and a paired control design (Skalski and McKenzie 1982).

Other specific data gaps and research needs pertaining to this assessment of treated wood include:

1. The influence of pH should be incorporated into the derivation of water quality standards for some metals, in particular, copper. Ample data is available for pH to be incorporated into copper water quality standards. Present standards incorporate water hardness to adjust standards. Water hardness and pH are generally positively correlated, however, the significant impact that pH has on copper speciation at neutral to acidic pH (< 8.0) should be included in establish water quality standards.
2. Sediment quality standards for metals and organics need to be normalized to those variables that control their biological availability and potential toxicity (TOC, AVS, percentage fines etc.). This is critical for freshwater and marine environments and has been a hot subject that continues to receive attention.
3. The relationship between hepatic lesions and reproductive biology of flat fish and sediment contaminants needs to be quantitatively evaluated to assess the combined and individual dose responses of PAH, chlorinated pesticides, PCBs, and trace metals. Early life stage exposure also needs to be evaluated when assessing impacts and developing sediment benchmarks.
4. A better understanding is needed of elevated tissue burdens of contaminants in biota and any adverse effect that can be associated with that burden. Body burdens of contaminants are important from the standpoint of direct impacts to organisms and the impact to consumers of those exposed organisms (e.g., juvenile salmon). The ability of aquatic organisms to metabolize contaminants is a significant factor in this aspect of assessment (particularly true for PAH).
5. While the utility of models for predicting effects of treated wood was not evaluated in detail, several models exist. Brooks (1994a, 1994b, 1995) has developed several models based on leaching rates to predict the environmental fate of treated wood contaminants. Empirical relationships between treated wood structures (amount of treated wood), age, and sediment burdens of contaminants related to the structures could be very helpful management tools.
6. No information was found in terms of assessing avoidance behavior of aquatic organisms to chemical contaminants released from treated wood. Given the temporal nature of metal leaching, avoidance of structures due to leached metals is an impact that can be mitigated, however, the long term release rates of PAH and the potential for olfactory interference is largely unknown, however, some research has been conducted with oil spills.

7. PAH undergo metabolic transformations creating intermediate compounds that are linked to carcinogenesis. Similarly, photo-oxidation may also produce similar transformations. These mechanisms need to be better understood to evaluate the risk of PAH in aquatic habitats.
8. Microbial and physical degradation processes for PAH need to be better understood to evaluate long-term risk of PAH in sediment. The role of inadvertent sediment ingestion as a route of exposure to contaminants needs additional evaluation.
9. There is a need to get a better understanding of diffusion rates of PAH from creosote treated pilings prepared under Best Management Practices. There are inconsistencies between microcosm studies and field studies involving creosote treated pilings with respect to monitoring of dissolved concentrations of PAH, accumulation in sediments, and mechanisms of transport (Goyette and Brooks 2000, Bestari et al. 1998)

Mitigation

Mitigation may be necessary where the environmental releases of contaminants from treated wood may cause adverse effects. Pawlak (1994) has prepared evaluation of alternatives to creosote treated wood that provides more detail on possible mitigation. Several strategies are presented with no specific order or preference. The following apply to new installations

1. Alternative material to treated wood could be used. Metal, concrete, or other composite materials could be used. Several surface coatings have been approved for aquatic applications on steel that meet leachate toxicity testing guidelines. Other possible impacts of alternative materials would need to be assessed.
2. If a selected species will occur at a construction site during a specific season, the work may be scheduled to avoid exposure to contaminants associated with treated wood by the sensitive species.
3. Treated wood may be further treated to further minimized release of chemical contaminants. While BMP treatments are design to minimize the release of contaminants into aquatic habitats, new products still release contaminants. Presoaking the products in water may further reduce leaching, however, this may not work for some applications. Where risk is minimal, the added reduction in risk may not justify the increase in cost. Application of a water sealant can also reduce the leaching rates of metals for above water portions of treated wood structures (Cooper et al. 2000).

Mitigation of effects for existing structures is more complicated. For example, if resource agencies determined that creosote piling were impacting spawning herring, there are several

approaches that could be taken. Sleeves could be placed over piling to isolate the structure and prevent spawning on the pilings. Another approach would be to install additional spawning surfaces for herring in the vicinity of the pilings. This may reduce the number of herring that spawned on the pilings and if the additional spawning structure was more suitable for spawning, may actually enhance spawning. A good understanding of herring spawning and habitat usage would be needed to evaluate these types of mitigation strategies.

Where existing treated wood installations may have impacts, one alternative is to remove the installation. For pilings where the wood is installed into the sediment, consideration has to be given to additional dispersal of contaminated sediment near the piling. In situations where sediment contaminated is elevated, an option would be to cut the piling off below sediment grade and leave the butt intact. Sediment that would backfill the hole would further isolate the piling remnant.

Small installations of treated wood are not likely to require any contaminant monitoring, however, large installations should require some level of monitoring to document potential impact of the facility to aquatic resources.

Glossary

Gravimetric Units Used in this Report

Many papers and reports have used different units to express similar terms. The following table provides a guide to these different terms and units that appear in this white paper.

Contaminant Concentrations in Tissue, Water or Sediment

µg/L (= ng/mL)	Micrograms per liter = nanograms per milliliter =	ppb	Part per billion
mg/L	Milligrams per liter =	ppm	Part per million
g/L	Grams per liter =	ppt	Part per thousand
µg/g = mg/kg	Micrograms per gram = milligrams per kilogram =	ppm	Part per million
ng/g	Nanograms per gram =	ppb	Part per billion

Wood Preservative Retention

pcf	Pounds per cubic foot
kg/m ³	Kilograms per cubic meter

Terms

abundance	number of a given species per area (or other taxonomic level of organization)
ACZA	ammoniacal copper zinc arsenate, denoting a treated wood process
alkalinity	water quality parameter that measures the acid neutralizing capacity of water (primarily a function of carbonate and bicarbonate and hydroxide content)
amphipod	freshwater or marine benthic arthropod commonly referred to as a scud in freshwater
anadromous	migratory life style (usually fish) where adults spawn in freshwater and juveniles mature into adults in marine environments
anthropogenic	derived from activities by mankind
As	arsenic
ascites	accumulation of body fluids as a result of disease or injury
avoidance	to deliberately move away from a stimulus
AVS	Acid Volatile Sulfide, a measurement of sulfides in sediment released when a sediment sample is incubated in cold hydrochloric acid (see SEM)
benchmark	a value assigned/proposed for a compound to indicate its relative hazard to an organism or ecosystem
bioaccumulation	the process by which an organism incorporates an element or compound into their body (usually from the water column)
bioconcentration	the processes of an organism to incorporate a compound or element from all environment routes (e.g., water, food, respiratory surfaces)
biodegradation	the process by which microbes or organisms breakdown larger more complex compounds

biomagnification	an ecological relationship where a contaminant accumulates to higher concentrations in tissue compared to 1) the exposure media or 2) organisms organized to increasing trophic level
biotransformation	the biochemical process where an organisms changes the structure of a compound to a different form that usually is more toxic than its predecessor
blastogenesis	the process where a cell multiplies and grows into a distinct and functioning mass
BMP	Best Management Practice
bulkhead	a marine or estuarine structure installed to interrupt and reduce wave action along shorelines
butadienes	a linier organic compound consisting of 4 carbon atoms (buta-) two double bonds (-diene)
carcinogenesis	the multistage process where by a tissue develops into an unregulated growing tissue mass
cation	positively charged element (e.g., Ca ⁺²)
CCA	chromated copper arsenate a name identifying a form of treated wood of which Type C is the most common formulation
chelation	the process of one compound binding or sequestering another element or compound
chironomid	group of aquatic insects commonly referred to as midges
chorion	the cell membrane of a fish egg
Cr	chromium
creosote	an organic material used as a wood preservative, high in polycyclic aromatic hydrocarbons
Cu	copper
cumulative impacts	the sum of all impacts from a specific action or event and others surrounding it in time and space
cytotoxicity	hazardous or poisonous to cells
diffusion	process where a constituent passively moves out of a material (solid, liquid or gaseous)
diversity	the presence (number) of different species (or other taxonomic levels of organization) in a given area
dolphin	a marine structure that consist of multiple pilings secured at the top and generally forming a "cone"
EEC	extreme effects concentration, a sediment quality benchmark
endocrine disruption	the process where an organic compound that is similar in structure to a hormone interferes with a the physiology of an organism
epibenthic fauna	benthic organisms that live on the sediment at the bottom of aquatic habitats
epibiota	organism living on the surface of a substance
ER-L	Environmental response - low; a sediment benchmark
ER-M	Environmental response - median; a sediment benchmark
ESA	Endangered Species Act
estuary	a body of water where freshwater is mixed with salt water
exposure	process used to define relationship between an organism and a toxicant bounded by concentration, duration, and mode (I.e., inhalation, ingestion etc.)
fines	a size based fraction of sediment including the smaller particles (< mm)
food chains	a series of different organism where one feeds upon the preceding species
geomorphometry	the structure (shape) of the ground or river, lake, estuary or ocean bottoms
guideline	a recommended value that should be followed, but does not carry a burden of enforcement
hardness	water quality parameter that quantifies the concentration of multivalent cations, primarily

	calcium and magnesium
hepatic	pertaining to the liver
HPAH	high molecular weight polycyclic aromatic hydrocarbons; 4 to 6 ring structures
humeral	pertaining to the circulation of fluids with a n organism (e.g., humeral antibodies
immuno-competence	the state of functioning of an organism's immune (disease resistance) system
immunotoxicity	the process where the functioning of immune system is reduce or compromised by an external agent
<i>in vitro</i>	within an artificial environment (test tube, culture dish)
<i>in vivo</i>	within a living organism
infaunal	animals residing in the sediment
K _{sp}	solubility product, an expression that denotes the solubility of a element or compound
LC _{xx}	an expression denoting a lethal concentration of a compound over a specified period of exposure (e.g., 48 hrs) for a portion (e.g., 50%) of a population; e.g., 48-hr LC ₅₀
leach	process where metals are dissolved and removed form a solid material (treated wood)
lipophillic	a characteristic of a compound where it is found in organic matrices (fat, adipose tissue) due to its lack of polar radicals
lipopolysaccharide	a class of sugar compounds (saccharide) combined with fat (lipid)
LPAH	low molecular weight polycyclic aromatic hydrocarbons; 2 to 3 ring structures
lysozyme	an enzyme that breaks down cell walls
microcosm	in ecology, a small experimental community of different organism used to assess ecosystem level effects
microlayer	a thin layer that forms on the water surface that accumulates buoyant biological and chemical materials
Microtox	A toxicity testing system based on the inhibition of light output from marine photoluminescent bacteria
mitogen	a compound that stimulates the growth of immuno-competent cells
MOU	Memorandum of understanding
MTCA	Model Toxics Control Act - WAC 173-240
narcosis	an effect of deadening the nervous system (reversible)
necrosis	death of tissue
neoplasm	a new spontaneous growth of tissue, usually cancerous
olfactory	pertaining to the sense of smell
oligochaete	Segmented freshwater worm
PAH	polycyclic aromatic hydrocarbons
pcf	pounds per cubic foot, used here in to designate retention of wood preservative
PEL	probable effects level - a sediment benchmark
pentachlorophenol	organic chlorinated compound used as a wood preservative
pH	measurement of acidity in water on a scale of 1 to 14 with lower values <7 become ore acidic
photooxidation	the exposure to ultraviolet light that causes an oxygen molecule to react and bind with an organic compound
phototoxicity	the process where by ultraviolet light causes oxidation of organic compounds to a more toxic entity than the parent compound
phylogenetic	pertaining to the evolution of life into discrete groups of levels of organization (i.e. species, family class etc.)
plankton	unicellular plant or animal life that lives in the water column
polychaete	segmented marine worm

precautionary principle	the application/consideration of additional safety factors when considering an action or event with insufficient information
retention	for treated wood, the amount of preservative left in the treated zone after treatment is complete
richness	a characteristic of a community based on number of species in a community and the total number of individuals in that community
s.e.	standard error
scoliosis	condition where there is curving of the spinal column
sediment	inorganic and organic material found at the bottom of lakes, streams and oceans
SEM	Simultaneously-Extracted Metals, the metals that are extracted with exposure to cold hydrochloric acid (see AVS)
standard	a promulgated value used to assess compliance of a law
TEC	threshold effects concentration, a sediment benchmark
TOC	total organic carbon
tPAH	total polycyclic aromatic hydrocarbons
TVS	total volatile solids
valence state	the charge (positive or negative) carried by a metal or compound, e.g., Cu ²⁺

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