Sulfide Effects on Aquatic Organisms
Literature Review
D. Podger

Summary

The first section of this paper provides a summary of the scientific literature on sulfide environmental fate, and the toxic effects of hydrogen sulfide, which includes benthic organisms, freshwater and marine fish, and eelgrass. The second section of the paper focuses on sulfide toxicity in the pore water of marine sediments, and the relevant toxicity information for organisms that may be potentially exposed to porewater in Puget Sound marine sediment.

Hydrogen sulfide is a hazardous substance that is released from organic matter, such as wood residue, that is decomposing in an anoxic environment. Although low levels of hydrogen sulfide may naturally occur in the sub-surface sediment, an excess amount of organic matter causes excess amounts of hydrogen sulfide to accumulate causing toxicity in the sediment and in the water column close to the sediment.

Sulfide toxicity is primarily from the hydrogen sulfide (H_2S) form of sulfide. Sulfide ions may bind with available metals and precipitate out of solution. There is no information in the scientific literature regarding toxicity of solid phase sulfides. Bioavailable sulfide may exist in the pore water and its toxicity depends on pH. At pH 7, about half of the porewater sulfide is in the toxic form H_2S, while at pH 8, only about 9% of the total sulfide will be in the toxic form. H_2S is volatile and easily oxidized (converted back into sulfate or other non-toxic forms in the presence of oxygen). Due to these properties, special protocols are needed to collect sulfide porewater samples that are representative of field conditions. Also laboratory sediment bioassays using standard protocols may not be effective at determining sulfide toxicity because the aeration reduces sulfide concentrations (Wang & Chapman 1999).

In the scientific literature, sulfide toxicity is described at different pH levels and using different measurements (H_2S versus total dissolved sulfide and µM versus mg/l). To evaluate toxicity in consistent units, all µM concentrations were converted to mg/l. Figure 1 shows the relationship between µM and mg/l total dissolved sulfide. The proportion of toxic H_2S compared to total dissolved sulfides varies by pH. Therefore, all toxicity values expressed as total dissolved sulfides were converted to approximate H_2S concentrations, based on chemical equilibrium equations and the pH reported in the literature (see figure 2). Table 1 describes all toxicity thresholds based on a common metric of mg/l hydrogen sulfide, which is independent of pH. However, most site data are collected as total dissolved sulfide in porewater. Therefore, the hydrogen sulfide thresholds must be converted to total dissolved sulfides based on the proportion of hydrogen sulfide found at a particular pH. If available, the actual pH value of the porewater can be used to make this conversion.

Table 1 shows a range of sulfide toxicity values based on total sulfide at a particular pH, and the equivalent hydrogen sulfide concentration. Sulfide toxicity varies by species and life stage. Larval forms of oyster, crab and sea urchins displayed abnormal development at very low concentrations of sulfide (0.1 to 0.5 mg/l sulfide at pH 8), but this life stage is usually in the water column, so may not have exposure to the sediment porewater. Amphipods were more sensitive to sulfide (LC_{50} 1.4 to 5.2 mg/l sulfide) than polychaetes and clams (LC_{50} 5.7 to 16 mg/l sulfide). Most of these studies were laboratory experiments where both sulfide and dissolved oxygen concentrations were maintained in the water column.

Sulfide has been demonstrated to be toxic to eelgrass (*Zostera marina*), but eelgrass has a physiological adaptation to compensate for low levels of sulfide. Reduced light and low oxygen levels in the water column prevent the eelgrass from compensating for sulfide, so can exacerbate sulfide toxicity to eelgrass. One Puget Sound study showed that *Zostera* beds were healthy below 1.6 mg/l sulfide, impaired at 6.4 mg/l sulfide, and completely absent at 32 mg/l sulfide (Elliot 2006).

Sulfide toxicity studies have been done on freshwater fish and show that fish can survive short exposures of 0.3 to 0.4 mg/l sulfide. Since hydrogen sulfide has a strong odor, fish are likely to avoid areas with sulfide, if possible, before reaching toxic levels. Studies on freshwater fish embryos showed decreased hatching success at low levels of sulfide. Based on this USEPA recommended a freshwater water quality criteria of 2 ug/l (0.002 mg/l) undissociated sulfide (H_2S). Some marine fish have higher tolerance for sulfide, such as the California killifish (LC_{50} 9.6 mg/l H_2S), while other marine fish are quite sensitive, such as the speckled sand dab, which can die after 2 hours of exposure to 0.4 mg/l H_2S (Bagarinao 1991).

Figure 1: Relationship of uM sulfides to mg/l sulfides. Since molecular weight of H_2S(34 g/mole), HS^- (33 g/mole) and S^{2-} (32 g/mole) are similar, this chart can be used to approximate the relationship of uM to mg/l for any of the chemical forms of sulfide.

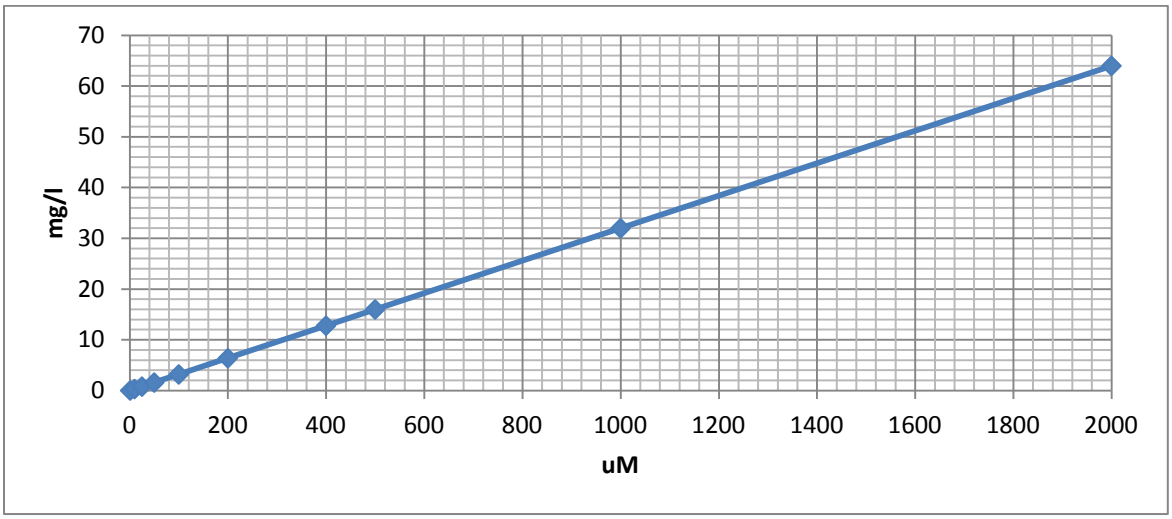


Figure 2: Proportion of H_2S species and SH^- species in total dissolved sulfides, depending on pH.

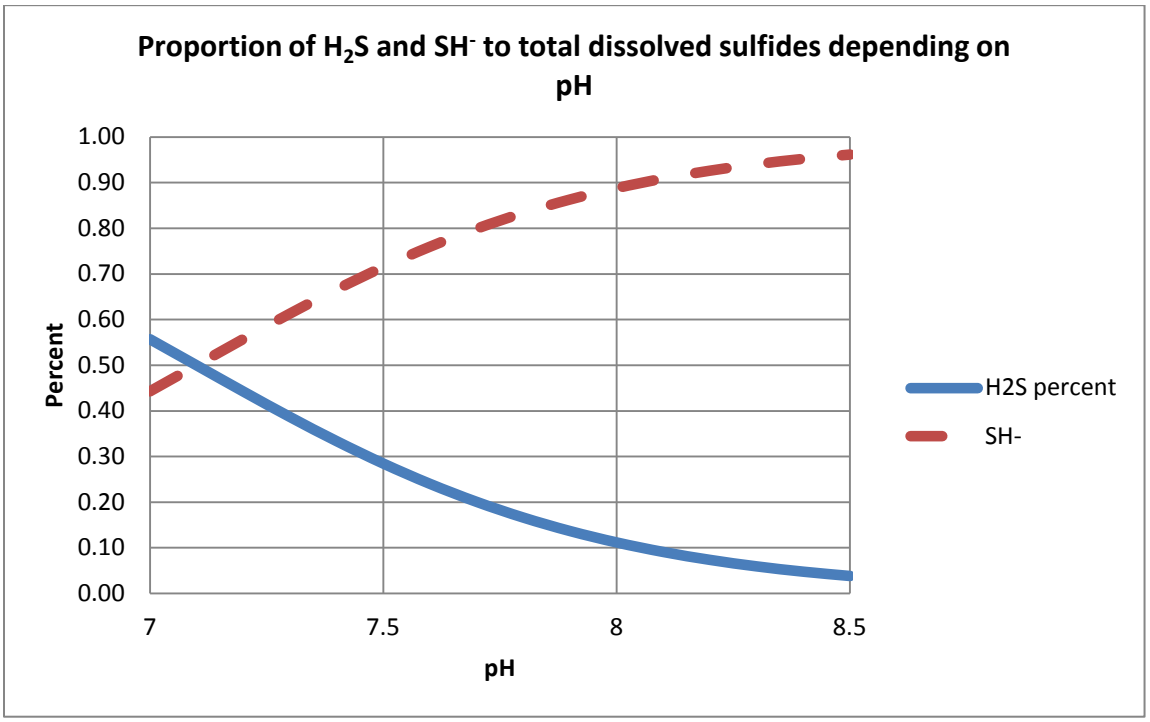


Table 1 Summary of sulfide toxicity values from scientific literature.

Organism	Total dissolved sulfides mg/l	pH	Estimated H_2S concentration mg/l	Endpoint	Reference
Mussel, *Mytilus* embryo	0.1	8	0.011	48-h EC50	Knezovich et al., 1996
Urchin *Strongylocentrotus, larvae*	0.13	8	0.015	48-h LOEC	Knezovich et al., 1996
Urchin *Strongylocentrotus, larvae*	0.19	8	0.021	48-EC50	Knezovich et al., 1996
Urchin Lytechinus pictus, mortality water column conc			0.048	LOEC, mortality from water column exposure	Thompson et al., 1991
Shrimp *Crangon*	0.64	8	0.072	1-h LT50	Vismann 1996
Amphipod *Rhepoxynius LOEC*	1.47	8	0.164	48-h LOEC	Knezovich et al., 1996
Amphipod *Rhepoxynius LC50*	1.6	8	0.179	48-h LC-50	Knezovich et al., 1996
Amphipod *Anisogammarus*			0.2	96-h LC50	Caldwell 1975
Mussel, *Mytilus*	1.9	8	0.212	96-h EC50	Abel 1976
Amphipod *Eohaustorius LOEC*	1.92	8	0.215	48-h LOEC	Knezovich et al., 1996
Amphipod *Eohaustorius LC50*	3.32	8	0.371	48-h LC-50	Knezovich et al., 1996
Chitharichthys stigameus, speckled sand dab			0.384	death in 2 hours	Bagarinao and Vetter, 1989

Organism	Total diss. sulfides mg/l	pH	Hydrogen sulfide mg/l	Endpoint	Reference
Crab *Cancer*, zoeae			0.5	96-h LC50	Caldwell 1975
Polychaete *Nereis*	5.76	8	0.644	24-D LT50	Vismann 1996
Oyster larvae development, *Crassostrea gigas*			0.56	Significant abnormal development after 2 hour H2S exposure	Caldwell 1975
Eelgrass *Zostera Marina,* reduced growth	6.4	*8*	0.716	No eelgrass in intertidal, reduced density in subtidal (200 uM)	Elliott et al., 2006
Crab *Cancer*, first instar			1.000	96-h LC50	Caldwell 1975
Fish, long-jawed mud sucker, Gillichthys mirabilis			1.024	96 hour LC_{50} at 16-20^{o}C	Bagarinao and Vetter, 1989
Fish, California killifish, Fundudlus parvipinnis			1.344	96 hour LC_{50} at 16-20^{o}C	Bagarinao and Vetter, 1989
Amphipod Corophium			1.400	24-h LC50	Caldwell 1975
Oyster *Crassostrea*			1.400	96-h LC50	Caldwell 1975
Polychaete Capitella	16	8	1.789	3-h LOEC in settlement time	Dubilier 1988
Clam *Arctica*	6.4	7.5	1.822	10-d LOEC	Oeschger et al., 1993
Urchin Lytechinus pictus, behavioral responses			2.900	Behavioral responses, sediment avoidance, time to turn over, growth reduction	Thompson et al., 1991
Urchin Lytechinus pictus, mortality 49 days			2.900	LOEC, mortality based on pore water concentrations	Thompson et al., 1991
Amphipod *Anisogammarus*			3.200	24-h LC50	Caldwell 1975
Eelgrass *Zostera Marina,* total inhibition	32	*8*	3.578	No eelgrass, Beggiatoa mats	Elliott et al., 2006
Amphipod *Gnorimosphaeroma*			5.200	96-h LC50	Caldwell 1975
Clam, *Macoma*			6.000	96-h LC50	Caldwell 1975
Fish, California killifish, Fundudlus parvipinnis			9.600	8 hour lethal concentration	Bagarinao 1991
Fish, long-jawed mud sucker, Gillichthys mirabilis			9.600	8 hour lethal concentration	Bagarinao 1991

underlined pH - pH was not given, assumed to be 8.0 for purposes of this exercise.

Sulfide production in a marine environment

Sulfide occurs in sediment due to microbial decomposition of organic matter in anoxic environment. Once oxygen and nitrates are depleted, bacteria use sulfate as the terminal electron receptor and produce sulfide as a byproduct. Sulfide is more common in marine environments than freshwater environments because marine water has significantly higher concentrations of sulfate that can be used by the bacteria.

Sulfide occurs naturally in the sediment horizon at the point where oxygen does not penetrate. Bioturbation or bioirrigation by sediment organisms may allow oxygen to penetrate deeper into the sediment horizon. The sulfide horizon is often characterized by black iron sulfide precipitates and the distinctive hydrogen sulfide smell (rotten eggs).

In areas with high organic loading, microbial activity can exceed the water body's capacity for oxygen supply, resulting in anoxia. High organic loading may result in increased sulfide production closer to the water/sediment interface, and higher concentrations of pore water sulfide.

Natural sources of sulfide in the aquatic environment include sulfur hot springs and geothermal vents, and hydrogen sulfide released from decay of non-anthropogenic organic matter. Human activities that can cause the release of hydrogen sulfide include petroleum refining, pulp and paper production, municipal sewage discharges, animal containment and manure handling, and other processes that discharge significant quantities of organic matter into the aquatic environment, such as sawmills, and canneries (ASTDR 2006).

Sulfide behavior in the environment

In water, sulfide exists in equilibrium of the following reaction.

$$H_2S \leftrightarrow H^+ + HS^- \leftrightarrow 2H^+ + S^{2-}$$

The pH of the water controls how much of each is present. H_2S is the most toxic form and is volatile. HS^- is ionized form, which may have some toxicity. The S^{2-} form rarely occurs at the pH of natural waters.

Sulfides can bind with metals and form insoluble precipitates such as iron sulfide and magnesium sulfide. The visible black in a sediment horizon is often iron sulfide precipitate. Thus the presence of sulfides can reduce soluble metals and their related toxicity (Wang 1999). There is no information in the scientific literature regarding toxicity of solid phase sulfide.

Hydrogen sulfide is volatile and accounts for the strong rotten egg smell of anoxic sediments. Volatile compounds can escape during sample collection, so handling and storage and may result in underestimating the actual *in situ* concentrations. Hydrogen sulfide also readily oxidizes, converting back into sulfate in the presence of oxygen. Samples must be protected from oxygen exposure and analyzed within a short amount of time to maintain sulfide levels (Chapman 2002).

Sulfide toxicity is greater in pore water than in the overlying water because concentrations of sulfide are higher and the pH is slightly lower so there is a greater proportion of the toxic form (Phillips 1997).

Oxygenated seawater can quickly oxidize hydrogen sulfide to a non-toxic form, with an oxidation ½-life of 20 minutes (Ostlund and Alexander 1963). In some cases, blue-green algae or other microorganisms colonize the surface of the sediment, and utilize hydrogen sulfide as an energy source creating an effective barrier to hydrogen sulfide entering the water column (Jorgensen and Fenchel 1974). This may also result in a diurnal variation in sulfide concentrations in the top 1 cm of the sediment, where higher sulfide concentrations accumulate at night when the algae do not photosynthesize and are reduced during the daylight hours (Hartman-Hansen 1978).

Vertical and horizontal gradients of sulfide concentrations are typically found in the sediment. The vertical gradients depend on the oxygen penetration in the sediment, which can also be affected by bioturbation or bioirrigation of benthic organisms. Horizontal spatial gradients may exist depending on organic content, water circulation patterns, and presence of bioturbating organisms.

Sulfide Toxicity

General

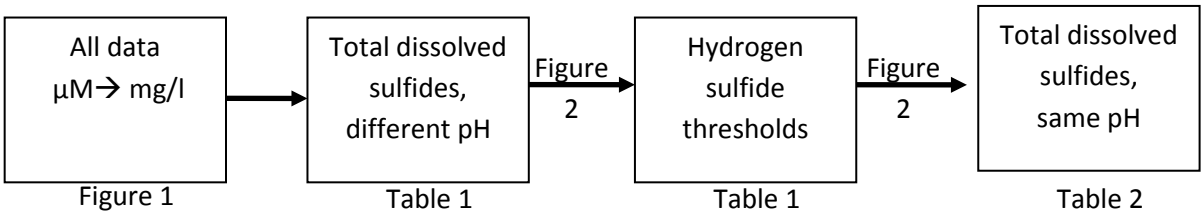
As stated previously, sulfide toxicity is dependent on pH because it is mainly the H_2S form of sulfide that is toxic. Lower pH water has a greater proportion of the toxic H_2S. At pH 7.0 about half of the aqueous sulfide exists as the toxic H_2S. At pH 8.0 only about 9% is H_2S. Toxicity values may be expressed as total sulfide for a particular pH, as shown in Table 1. (Wang 1999) The proportion of toxic hydrogen sulfide can be approximated by the equilibrium equation:

$[H_2S] = [\text{total } S^{2-}] \times (1-(1/(1 + 10^{(pK_a - pH)})))$ pKa = 7.1 (Phillips 1997)

Based on this equation, Figure 2 shows the proportion of HS^- and H_2S between pH 7 and pH 8.5, which encompass the pH range typically found in aquatic environments and porewater.

In the scientific literature reviewed for this paper, toxicity values were reported in various units, and measured different forms of sulfide. To develop a toxicity curve, the toxicity thresholds needed to be converted into units that could be compared to each other. First, all values were converted from µM to mg/l. Figure 1 shows the relationship between µM and mg/l. Some toxicity values were reported as the H_2S form, others as total dissolved sulfides at a particular pH. The equilibrium equation above was used to estimate toxic H_2S concentrations from total dissolved sulfides, as shown in Table 1. Once all toxicity values were in consistent units, the estimated total dissolved sulfide toxicity thresholds could be calculated at a particular pH using the equilibrium proportion of the toxic form, H_2S. Table 2 and Figure 4 shows toxicity thresholds as total dissolved sulfide concentrations at 2 different pH values that are typical for marine sediment pore water.

This diagram illustrates the steps described previously to report toxicity values that could be compared to environmental data. The diagram also describes the tables and figures in this paper where the information can be found.



Effects of H_2S are similar to hydrocyanic acid. Sulfide can fix iron in cytochrome and therefore reduce the oxygen intake of cells, especially nerve cells. The action of H_2S is that it first stimulates and then paralyzes nerve cells. The actions are reversible (Evans 1967). H_2S has also been shown to cause developmental abnormalities in early larval stages, such as abnormal shell development in oyster embryos (Caldwell 1975). H_2S affects cytochrome c oxidase and other enzymes, oxygen transport proteins, cellular structures, and consequently the physiological functions of organisms (Bagarinao 1992).

Toxicity thresholds for H_2S have been harder to develop than for other chemicals. Traditional sediment bioassays are aerated and therefore oxidize and volatilize H_2S and so are not always effective at determining sulfide toxicity. In addition, since it can be difficult to maintain stable levels of sulfide and oxygen, some effects may be due to oxygen depletion rather than sulfide toxicity. Some experiments have automated flow through systems and were able to maintain adequate oxygen levels, stable sulfide levels and constant pH to isolate the effects of sulfide alone (Wang 1999).

There are a wide range of sulfide toxicity levels, depending on the species. Some organisms have anaerobic respiration capabilities and are not affected by the presence of sulfides. Others are less affected because they get water from the overlying water column, where sulfide levels are lower (Caldwell 1975). Bagarinao explores a variety of adaptations against sulfide toxicity including symbiotic relationships with sulfide-oxidizing bacteria, anaerobic metabolism, and detoxification of sulfide by intracellular processes (Bagarinao 1992). In all the studies shown here, however, hydrogen sulfide was shown to be toxic to aquatic organisms.

Benthic & Epibenthic Invertebrate Toxicity

Caldwell (1975) tested a variety of organisms for sulfide toxicity and found LC_{50} concentrations ranged from 0.2 mg/l to 6.0 mg/l H_2S, with the most sensitive organisms being an amphipod. The stage of development was also an important consideration as bivalve larvae were sensitive to H_2S resulting in abnormal development. Seven day old velligers and bivalve adults, however, were relatively sulfide tolerant. Generally, amphipods and larval stages were most sensitive and bivalves and isopods were less sensitive to H_2S.

Caldwell tested amphipods, an isopod, and *Macoma* clams using a flow thru apparatus for up to 96 hours exposure with a freshly mixed seawater and sulfide solution. Five different sulfide concentrations were tested. Oyster larvae were too small to test in the flow-through apparatus, so were tested in static cultures limited to 2-hours of exposure to minimize oxygen depletion and sulfide oxidation, followed by exposure to normal seawater. The results are presented in Table 1. Different organisms showed different levels of sensitivity to H_2S with a 96-hour LC_{50} ranging from 0.2 mg/l (amphipod *Anisogammarus*) to 6.0 mg/l (*Macoma* clam).

In the Caldwell study, oyster larvae development was also a sensitive endpoint, where 2-hour exposure of 0.56 mg/l H_2S resulted in abnormal development in the majority of larvae. However, the oyster larval tests were performed at increased temperature (26^{o}C), which has shown to increase sulfide toxicity sensitivity in other species. Oyster larvae were much more tolerant of H_2S once they had developed to 7-day old velligers (became inactive after 2-hour exposure to 3.2 mg/l sulfide, but recovered after 24 hours). Crab (*Cancer magister*) first instar zoeae were also sensitive to hydrogen sulfide exposure with 50% mortality after 24 hours exposure at 0.7 mg/l and slightly less sensitivity once they are post larval crabs. However, oyster larvae and first instar crab zoeae are planktonic and so less likely to be found in contact with the sediment pore water. Adult bivalves are some of the most sulfide tolerant organisms.

Knezovich (1996) also found that mussel and sea urchin larvae development were the most sensitive endpoints with effects at 0.1 to 0.2 mg/l total dissolved sulfide, although larvae are Planktonic and not likely to have much exposure to sediment pore water. Amphipod mortality occurred at slightly higher concentrations of sulfide. Knezovich tested four organisms; mortality for two amphipods *(Rhepoxynius abronius* and *Eohaustorius estuarius)* and embryo development in pore water *(Mytilus edulis* and *Strongylocentrotus purpuratus*). The study design was a 48-hour exposure using flow through test apparatus that maintained constant levels of sulfide, pH and dissolved oxygen. Knezovich found that larval development was the most sensitive endpoint for both purple sea urchin embryos (*Strongylocentrotus purpuratus*) and bay mussels (*Mytilus edulis*) with an total dissolved sulfide EC_{50} of 0.1 mg/l for *M. edulis* and 0.19 mg/l for *S. purpuratus*, and total inhibition of normal development at 0.25 mg/l for *M. edulis* larvae and 0.64 mg/l for *S. purpuratus* larvae. Amphipod survival was less sensitive to sulfide toxicity, with affects beginning at about 1.5 to 1.9 mg/l total dissolved sulfides and estimated total sulfide LC_{50} of 1.6 mg/l for *Rhepoxynius abronius* and 3.3 mg/l for *Eohaustorius estuarius*.

Fish toxicity

The USEPA Redbook (1975) summarizes available data on sulfide toxicity to fish at the time of its publication. The publication states that:

- The degree of hazard exhibited by sulfide to aquatic animal life is dependent on the temperature, pH and dissolved oxygen. At lower pH values a greater proportion is in the form of the toxic undissociated H_2S.
- When the pH is neutral or below, or when dissolved oxygen levels are low but not lethal to fish, the hazard from sulfides is exacerbated.

- Fish exhibit a strong avoidance reaction to sulfide, and if there is an escape route they are likely to be repelled by the odor before they are harmed.

Past data indicate that freshwater fish can survive short exposures of 0.3 to 0.4 mg/l H_2S (Van Horn 1958, Boon and Follis 1967, Theede et al., 1969). USEPA summarized a number of studies on freshwater fish that showed safe levels of H_2S between 2 ug/l (0.002 mg/l) and 15 ug/l (0.015 mg/l) for the freshwater species. USEPA recommended that concentrations exceeding 2.0 ug/l (0.002 mg/l) of undissociated H_2S would constitute a long-term hazard to fish. (USEPA 1976). Although USEPA has recommended water quality criteria of 2 ug/l H_2S for both freshwater and marine water (USEPA 1975), the state of Washington has not adopted this recommended criteria as a water quality standard. (Cheryl Niemi, personal communication).

Knezovich (1996) noted that sulfide concentrations are typically higher in marine environments, due to the abundance of sulfate in the water. Bagarinao (1992) also showed that generally marine fish are more tolerant of sulfide than freshwater fish, but there was a wide range of sulfide tolerance in marine fishes. The salt marsh fish, California kiilifish (*F. Parvipinnis*) is highly tolerant of sulfide (9.6 mg/l H_2S for an 8 hour lethal concentration)(Bagarinao 1991). The speckled sand dab (*Chithariachthys stigameus*), which resides in coastal areas, is more sensitive, with death occurring after 2 hours of 0.384 mg/l H_2S. (Bagarinao and Vetter, 1989)

….

Eelgrass and sulfide toxicity

Sulfide has been demonstrated to be toxic to eelgrass *Zostera marina*. If *Zostera* is in areas with high levels of oxygen in the water column and high photosynthesis rates (clear water, no shading), it can deliver oxygen to the roots and mitigate for low levels of sulfide. Reduced photosynthesis makes sulfide toxic to eelgrass at lower concentrations. Sulfide may result in reduced plant growth or plant death. Porewater sulfide above 32 mg/l is associated with no eelgrass plants and filamentous algal mats. Porewater sulfide below 1.6 mg/l has been associated with healthy eelgrass growth in one location. Porewater sulfide above 6.4 mg/l has been associated with absence of eelgrass in the intertidal zone and reduced density in the subtidal zone(Elliot 2006).

Zostera marina eelgrass are adapted to live in mildly anaerobic conditions. The eelgrass have a lacunar system to deliver oxygen from the shoots to the roots and rhizomes in the anoxic sediments, thereby oxidizing the sulfide near the root zone and preventing sulfide intrusion into the plant tissue (Holmer 2005). The oxygen in the eelgrass may be derived from photosynthesis (Smith and Pregnall 1985), or from water column oxygen (Pedersen 2004). If the water column is anoxic at times, or photosynthesis is reduced due to shading or water clarity, the eelgrass is susceptible to sulfide toxicity at lower concentrations (Holmer 2001).

Goodman (1995) listed several mechanisms of sulfide toxicity in plants including inhibition of nutrient uptake, decrease in function of respiratory root mettalo-enzymes, and decreases in ATP that may affect

other metabolic processes, including photosynthesis. Holmer (2001) further demonstrated that *Zostera* have decreased rates of photosynthesis and decreased shoot biomass with increases in sulfide concentrations and anoxic water column conditions. With concentrations of sulfide between 100 µM (3.2 mg/l) and 1,000 µM (32 mg/l), the plants had 80% reduction in photosynthesis and 55% decrease in shoot biomass. Goodman (1995) showed that sulfide concentrations of 400-800 µM can reduce photosynthesis maximum by about 30%, and sulfide concentrations of 800-1000 µM can reduce photosynthesis by about 50%. So the presence of sulfide can itself reduce photosynthesis reactions, thereby reducing the plant's ability to mitigate for the sulfide.

Sulfide toxicity from exposure to marine pore water in Puget Sound

To use literature values to evaluate potential injury from hydrogen sulfide concentrations in pore water, two adjustments were made to the list of marine organisms toxicity thresholds.

- First, some species were removed from the list because either they are species or life stages that would not be typically exposed to sediment pore water, or they are species that are not commonly found in Puget Sound nor potential surrogates for Puget Sound species.
- Second, the hydrogen sulfide toxic thresholds are converted to estimated total dissolved sulfides concentrations based on equilibrium equations. Marine sediment pore water is typically more acidic than the overlying water (Phillips 1997). Total dissolved sulfide toxicity curves are presented in Figure 4 for 2 pH levels that would be typical for marine sediment pore water (7.6-7.9).

Table 2 and Figure 4 summarize the scientific literature for marine aquatic organisms that may be exposed to sulfide in sediment porewater. Table 2 presents the toxicity thresholds as H_2S concentrations, as well as estimated total dissolved sulfides concentrations at two pH levels. Figure 4 has a graph of the porewater toxicity values expressed only as total dissolved sulfides at the two pH levels, which are typical pH values found in marine sediment pore water.

If sediment pore water concentrations are measured at a particular site, the site-specific information can be used to estimate total dissolved sulfide concentrations from the hydrogen sulfide toxicity values.

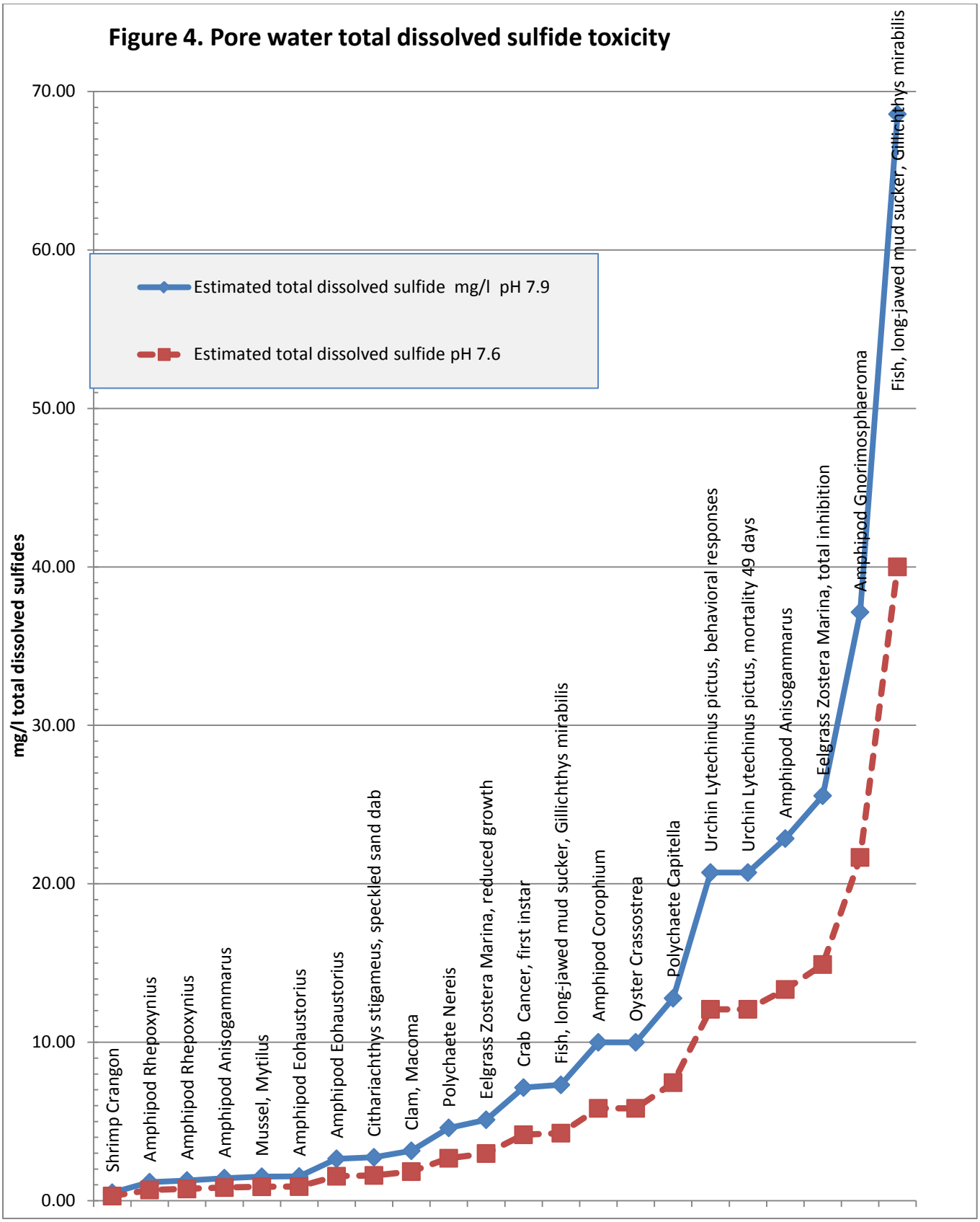


Figure 4. Pore water total dissolved sulfide toxicity
mg/l total dissolved sulfides
70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
Estimated total dissolved sulfide mg/l pH 7.9
Estimated total dissolved sulfide pH 7.6
Shrimp Crangon
Amphipod Rhepoxynius
Amphipod Rhepoxynius
Amphipod Anisogammarus
Mussel, Mytilus
Amphipod Eohaustorius
Amphipod Eohaustorius
Citharichthys stigameus, speckled sand dab
Clam, Macoma
Polychaete Nereis
Eelgrass Zostera Marina, reduced growth
Crab Cancer, first instar
Fish, long-jawed mud sucker, Gillichthys mirabilis
Amphipod Corophium
Oyster Crassostrea
Polychaete Capitella
Urchin Lytechinus pictus, behavioral responses
Urchin Lytechinus pictus, mortality 49 days
Amphipod Anisogammarus
Eelgrass Zostera Marina, total inhibition
Amphipod Gnorimosphaeroma
Fish, long-jawed mud sucker, Gillichthys mirabilis

Table 2. Toxicity values from the literature converted to total dissolved sulfides concentrations at pH 7.6 and pH 7.9, which are in the range of typical marine porewater pH values.

Organism	Estimated H_2S concentration mg/l	Estimated total dissolved sulfide mg/l at pH 7.9	Estimated total dissolved sulfide mg/l at pH 7.6	Endpoint	Reference
Shrimp *Crangon*	0.072	0.51	0.30	1-h LT50	Vismann 1996
Amphipod *Rhepoxynius*	0.164	1.17	0.68	48-h LOEC	Knezovich et al., 1996
Amphipod *Rhepoxynius*	0.179	1.28	0.75	48-h LC-50	Knezovich et al., 1996
Amphipod *Anisogammarus*	0.2	1.43	0.83	96-h LC50	Caldwell 1975
Mussel, *Mytilus*	0.212	1.52	0.89	96-h EC50	Abel 1976
Amphipod *Eohaustorius*	0.215	1.53	0.89	48-h LOEC	Knezovich et al., 1996
Amphipod *Eohaustorius*	0.371	2.65	1.55	48-h LC-50	Knezovich et al., 1996
Chitariachthys stigameus, speckled sand dab	0.384	2.74	1.60	death in 2 hours	Bagarino and Vetter, 1989
Clam, *Macoma*	0.442	3.15	1.84	96-h LC50	Caldwell 1975
Polychaete *Nereis*	0.644	4.60	2.68	24-D LT50	Vismann 1996
Eelgrass *Zostera Marina,* reduced growth	0.716	5.11	2.98	No eelgrass in intertidal, reduced density in subtidal (200 uM)	Elliott et al., 2006

Organism	Estimated H_2S concentration mg/l	Estimated total dissolved sulfide mg/l at pH 7.9	Estimated total dissolved sulfide mg/l at pH 7.6	Endpoint	Reference
Crab *Cancer*, first instar	1.000	7.14	4.17	96-h LC50	Caldwell 1975
Fish, long-jawed mud sucker, Gillichthys mirabilis	1.024	7.31	4.27	96 hour LC_{50} at 16-20^{o}C	Bagarino and Vetter, 1989
Amphipod Corophium	1.400	10.00	5.83	24-h LC50	Caldwell 1975
Oyster *Crassostrea*	1.400	10.00	5.83	96-h LC50	Caldwell 1975
Polychaete Capitella	1.789	12.78	7.45	3-h LOEC in settlement time	Dubilier 1988
Urchin Lytechinus pictus, behavioral responses	2.900	20.71	12.08	Behavioral responses, sediment avoidance, time to turn over, growth reduction	Thompson et al., 1991
Urchin Lytechinus pictus, mortality 49 days	2.900	20.71	12.08	LOEC, mortality based on pore water concentrations	Thompson et al., 1991
Amphipod *Anisogammarus*	3.200	22.86	13.33	24-h LC50	Caldwell 1975
Eelgrass *Zostera Marina,* total inhibition	3.578	25.56	14.91	No eelgrass, Beggiatoa mats	Elliott et al., 2006
Amphipod *Gnorimosphaeroma*	5.200	37.14	21.67	96-h LC50	Caldwell 1975
Fish, long-jawed mud sucker, Gillichthys mirabilis	9.600	68.57	40.00	8 hour lethal concentration	Bagarino 1991

References

Abel, P.D. (1976) Effect of some pollutants on the filtration rate of *Mytilus*. Mar. Pollut. Bull. 7, 228-231.

ATSDR (2006) Agency for Toxic Substance and Disease Registry (ATSDR) Toxicological Profile for Hydrogen Sulfide. PB2007-100675. July 2006. www.atsdr.cdc.gov/ToxProfiles/tp114.pdf

Boon, C.W., Follis, B.J. (1967) Effects of hydrogen sulfide on channel catfish. Trans. Amer. Fish. Soc., 96: 31.

Caldwell, R.S., (1975) Hydrogen sulfide effects on selected larval and adult marine invertebrates. Completion Report on Project No. A-020-ORE, Research performed for the Office of Water Research and Technology, United States Dept. of Interior. Water Resources Research Institute, Oregon State University, Corvallis, OR. April 1975.

Chapman, P.M. F., Wang, J.D., Germano, G. Batley (2002). Pore water testing and analysis: the good, the bad, and the ugly. Marine Pollution Bull. 44, 359-366.

Cline, J.D., Richards, F.A. (1969) Oxygenation of hydrogen sulfide in sea water at constant salinity, temperature, and pH. Env. Sci. Technol. 3, 838-843.

Dublier, N. (1988) H2S – A settlement cue or toxic substance for *Capitella sp. I* larvae? Biol. Bull. 174, 30-38.

Elliott, J.K., Spear, E., Wyllie-Echeverria S. (2006) Mats of *Beggiatoa* bacteria reveal that organic pollution from lumber mills inhibits growth of *Zostera marina.* Marine Ecology 27, 372-380.

Evans, C.L. (1967) The toxicity of hydrogen sulphide and other sulphides. Quart. J. Exp. Physiol. 52, 231-248.

Goodman, J.L., Moore, K.A., Dennison, W.C. (1995) Photosynthetic responses of eelgrass (Zostera marina) to light and sediment sulfide in a shallow barrier island lagoon. Aquatic Botany 50, 37-47.

Hartmann Hansen, M., Ingvorsen, K, Jorgensen, B.B., (1978) Mechanisms of hydrogen sulfide release from coastal marine sediments to the atmosphere. Limonol. & Oceanography 23, 68-76.

Holmer, M., Frederiksen, M.S., Mollegaard, H. (2005). Sulfur accumulation in eelgrass (*Zostera marina*) and effect of sulfur on eelgrass growth. Aquatic Botany 81, 367-379.

Holmer, M., Bondgaard, E.J. (2001) Photosynthetic and growth response of eelgrass to low oxygen and high sulfide concentrations during hypoxic events. Aquatic Botany 70, 29-38.

Jorgensen, B.B., Fenchel, T. (1974) The sulfur cycle of a marine sediment model system. Mar. Biol. 24, 189-201.

Knezovich J.P., Steichen, D.J., Jelinski, J.A., Anderson, S.L. (1996) Sulfide tolerance of four marine species used to evaluate sediment and pore-water toxicity. Bull Environ. Contamin. Toxicol. 57, 450-457.

Koch, E.W. (2001) Beyond light: Physical, geological, and geochemical parameters as possible submersed Aquatic Vegetation Habitat Requirements. Estuaries 24, 1-17.

Oeschger, R., Sotrey, K.B. (1993) Impact of anoxia and hydrogen sulphide on the metabolism of *Arctica islandica* (Bivalvia). J. Exp. Mar. Biol. Ecol. 170, 213-226.

Ostlund, H.G., Alexander, J. (1963) Oxidation rate of sulfide in sea water, a preliminary study. J. Geophys. Res. 68, 3995-3997.

Pederesen, O., Binzer, T., Borum J. (2004) Sulphide intrusion in eelgrass *(Zostera marina).* Plant, Cell and Environ. 27, 595-602.

Phillips, B.M., Anderson, B.S., Hunt, J.W. (1997) Measurement and Distribution of Interstitial and Overlying Water Ammonia and Hydrogen Sulfide in Sediment Toxcitiy Tests. Marine Environ. Research 44, 117-126.

Pregnall, A.M., Smith R.D., Kursar, T.A., Alberte, R.S. (1984) Metabolic adaptation of *Zostera marina* (eelgrass) to diurnal periods of root anoxia. Marine Biology 83, 141-147.

Smith, R.D., Pregnall, A.M., Alberte, R.S. (1988). Effects of anaerobiosis on root metabolism of *Zostera marina* (eelgrass): implications for survival in reducing sediments. Marine Biology 98, 131-141.

Terrados, J., Duarte, C.M., Kamp-Nielsen, L., Agawin, N.S.R., Gacia, E., Lacap, D., Fortes, M.D., Borum, J., Lubanski, M., Greve, T. (1999) Are seagrass growth and survival constrained by the reducing conditions of sediment? Aquatic Botany 65, 175-197.

Theede, H., et al., (1969) Studies on the resistance of marine bottom invertebrates to oxygen deficiencies and hydrogen sulfide. Mar. Biol. 2: 325.

USEPA (1976) Quality Criteria for Water USEPA. The Red Book. USEPA Publication PB-263-943. pp 410-416.

Van Horn, W.M. (1958) The effect of pulp and paper mill wastes on aquatic life. Proc. Ontario Indust. Waste Conf. 5: 60.

Vismann, B. (1990) Sulfide detoxification and tolerance in *Nereis (Hediste) diversicolor* and *Nereis (Neanthes) virens* (Annelida:Polychaeta) Mar. Ecol. Prog. Ser. 59, 299-238.

Vismann, B. (1996) Sulfide species and total sulfide toxicity in the shrimp *Crangon crangon*. Jour. Exp. Mar. Biol. Ecol. 204, 141-154.

Wang, F., Chapman, P.M (1999) Biological implications of sulfide in sediment – A review focusing on sediment toxicity. Environ. Tox. and Chem. 18, 2526-2532.