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Risk of Pore Water Hydrogen Sulfide Toxicity in Dredged Material Bioassays

by Jerre G. Sims, David W. Moore

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Prepared for Headquarters, U.S. Army Corps of Engineers

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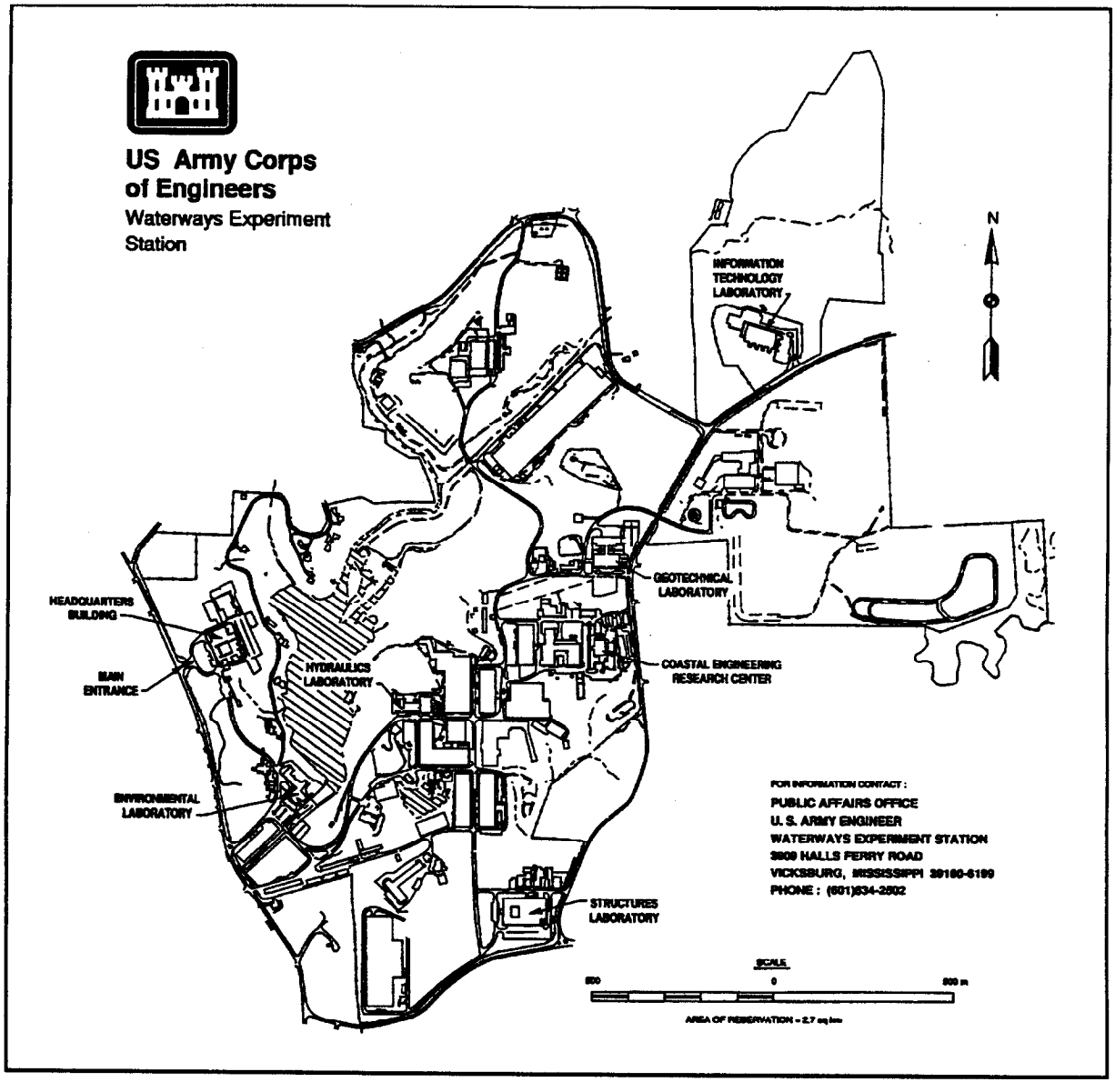

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Report Summary

Risk of Pore Water Hydrogen Sulfide Toxicity in Dredged Material Bioassays (MP D-95-4)

ISSUE: In the past, hydrogen sulfide has not been treated as a contaminant of concern; but because it can exert toxicity effects, based on whole sediment and elutriate toxicity tests, the potential of hydrogen sulfide toxicity was evaluated.

RESEARCH: To evaluate the potential of hydrogen sulfide toxicity in dredged material bioassays, a literature review and survey were conducted. Data collected included pore water exposure concentrations and effects concentrations of laboratory studies.

SUMMARY: The comparison of reported exposure and effects concentrations suggests a strong potential for hydrogen sulfide toxicity in dredged material bioasssays.

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Preface

The work reported herein was conducted by the U.S. Army Engineer Waterways Experiment Station (WES) for Headquarters, U.S. Army Corps of Engineers (HQUSACE). Financial support was provided by HQUSACE through the Dredging Operations Technical Support (DOTS) Program, Work Unit "Influence of Non-contaminant Sediment Characteristics on Dredged Material Bioassays." The DOTS Program is managed through the Environmental Effects of Dredging Programs, Dr. Robert M. Engler, Manager. Mr. Thomas R. Patin was Program Manager for DOTS.

The report was prepared by Ms. Jerre G. Sims and Dr. David W. Moore, Environmental Processes and Effects Division (EPED), Environmental Laboratory (EL), WES.

Technical review was provided by Drs. Todd Bridges and Tom Dillon, EPED.

The work was performed under the general supervision of Dr. Bobby L. Folsom, Jr., Chief, Fate and Effects Branch, EPED. The Chief of EPED was Mr. Donald L. Robey, and the Director of EL was Dr. John W. Keeley.

At the time of publication of this report, Director of WES was Dr. Robert W. Whalin. Commander was COL Bruce K. Howard, EN.

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1 Purpose

Hydrogen sulfide (H_2S) is a highly toxic, naturally occurring constituent of sediment pore water. It is not treated as a contaminant of concern for the regulatory evaluation of dredged material since it undergoes rapid oxidation and dilution during dredging and disposal. However, because dredged material is evaluated using effects-based testing (i.e., whole sediment and elutriate toxicity tests), there is the potential for H_2S to exert toxicity and confound the regulatory decision-making process. This report evaluates the potential for hydrogen sulfide toxicity in dredged material bioassays.

2 Approach

To characterize the potential for hydrogen sulfide toxicity in dredged material bioassays, two types of information are required: (a) exposure concentrations (i.e., concentrations of hydrogen sulfide reported for sediment pore water) and (b) effects concentrations (i.e., levels of hydrogen sulfide shown to induce adverse effects in aquatic species). To collect exposure information, an extensive literature survey was conducted of published pore water concentrations of hydrogen sulfide. In addition, information was requested on pore water concentrations of hydrogen sulfide associated with dredged material from every United States Army Corp of Engineers (USACE) Division and District. Information on exposure concentrations included reported concentration units, associated physical/chemical parameters (e.g., salinity, grain size, and total organic carbon), depth of sediment collection, and methods of pore water collection and analysis. Literature was also reviewed for concentrations of hydrogen sulfide shown to produce adverse effects in laboratory studies with aquatic species. This effects information included end point (e.g., lethality, growth, and reproduction), the concentration resulting in lethality or other effects in 50 percent of the test organisms (i.e., the LC_{50} or EC_{50}, respectively), the no observable effects concentration (NOEC), and the lowest observable effects concentration (LOEC) reported.

3 Background

Environmental Distribution

Hydrogen sulfide results from bacterial reduction of sulfates and the putrefaction of proteins. Hydrogen sulfide is associated with hypoxic environments (e.g., dissolved oxygen <1.0 mg/ℓ) and rapidly oxidizes under aerobic conditions (Bagarinao 1992). Sewage, naturally decomposing organic matter, and some industrial wastes (e.g., effluent from pulp mills, tanneries, and chemical plants) are major sources of sulfides (U.S. Environmental Protection Agency (USEPA) 1986). Unionized hydrogen sulfide (H_2S) occurs in interstitial waters where it exists in equilibrium with the hydrogen sulfide anion (HS^-) and the bisulfide anion ($S^=$). The ratio of these three forms is a function of pH, temperature, and ionic strength (Goldhaber and Kaplan 1974; Millero, Plese, and Fernandez 1988).

Toxicity

Hydrogen sulfide is a metabolic poison that is lethal to most invertebrates at concentrations <0.1 mM/ℓ (Colby and Smith 1967; Oseid and Smith 1974a,b; Smith et al. 1976a; Thompson et al. 1991; Knezovich et al. 1994). The toxicity of hydrogen sulfide results primarily from the undisassociated H_2S molecule that freely diffuses across membranes (National Research Council 1979; Pearson and Rosenberg 1978; Bagarinao 1992). At pH 7, H_2S and HS^- predominate. Decreasing pH, dissolved oxygen, and/or increasing temperature increases the proportion of undisassociated H_2S and enhances toxicity (Theede 1973; USEPA 1986).

Hydrogen sulfide exerts its toxicity by forming sulfides with the active groups of different metalloenzymes and blood pigments (e.g., the Fe component of cytochrome oxidase can be tied up as a sulfide, thereby interrupting cellular respiration) (Miron and Kristensen 1993). Some organisms, especially benthic invertebrates, are extremely tolerant of H_2S and will preferentially select sulfidic habitats (Meyers, Powell, and Fossing 1988; Powell, Crenshaw, and Rieger 1979). Other aquatic animals are able to tolerate sulfidic conditions for short periods of time (Theede et al. 1969; Baird, Wilson, and Miliken 1973; Bagarinao and Vetter 1989). There are also some animals that respond

behaviorally to avoid (e.g., tube building) or escape sulfidic conditions. Some animals that tolerate sulfidic conditions have been shown to possess physiological mechanisms to immobilize H_2S via sulfide-binding proteins or persulfides. Bound sulfides are then removed by excretion and/or detoxified (Powell, Crenshaw, and Rieger 1979; Arp and Childress 1983; Powell and Somero 1983; Bagarinao and Vetter 1989; Bagarinao 1992).

Sample Collection and Analytical Techniques

There are a number of methods for the collection and analysis of H_2S in sediment pore water. The three most common methods are centrifugation, squeezing, and the use of in situ diffusion samplers. With the centrifugation method, aliquots of sediment are centrifuged usually at low speed (e.g., 1,800 × g) for a set period of time (usually 15-30 min). Following centrifugation, pore water is decanted. The squeezer method uses a hydraulic or pneumatic collection device to squeeze an undisturbed sediment sample (core) under pressure, forcing pore water from the sediment through a filter membrane into a collection vessel. Diffusion samplers rely on diffusion over time through semipermeable membranes of a container placed directly in the sediment. Other collection methods include use of syringes, "sippers," and pipette samplers. These methods involve inserting a collection device into the sample and extracting the pore water through a filter under vacuum. Since H_2S rapidly oxidizes in the presence of oxygen, samples must be extracted under hypoxic conditions, analyzed as soon as possible, and preferably collected and stored under anoxic conditions (i.e., replacing oxygen with nitrogen or an inert gas such as argon).

Three commonly used methods for the chemical analysis of sulfide in water include a spectrophotometric procedure using methylene blue, iodometric titration, and a potentiometric method. The methylene blue method (allows for short-term storage of samples prior to analysis) is used for concentrations up to 580 µM/ℓ (20 mg/ℓ) total sulfide. Samples with higher concentrations must be diluted prior to analysis. Photometric determinations are made with a spectrophotometer. The iodometric titration method is recommended for freshly collected samples with concentrations of total sulfide >30 µM/ℓ (>1 mg/ℓ). This method requires samples that are free of interferences (e.g., thiosulfate, sulfite, iodine, and various organic and soluble substances). A third method, the potentiometric method, uses a silver electrode and a reference electrode to determine total sulfide concentration (American Public Health Association (APHA) 1985). Several useful qualitative techniques include the use of lead acetate paper or silver foil that becomes progressively darker with increasing concentrations of H_2S. The antimony test gives a yellow color if total sulfide concentrations of >1.47 µM/ℓ (>0.5 mg/ℓ) are present.

4 Exposure Data

Pore water concentrations of hydrogen sulfide were obtained from 25 publications covering 50 sites in freshwater, estuarine, and marine environments around the world. No pore water concentrations of hydrogen sulfide were reported by USACE Divisions and Districts, and only a single study (Moore and Dillon 1993) reported hydrogen sulfide concentrations for dredged material. Sample locations are shown in Figure 1.

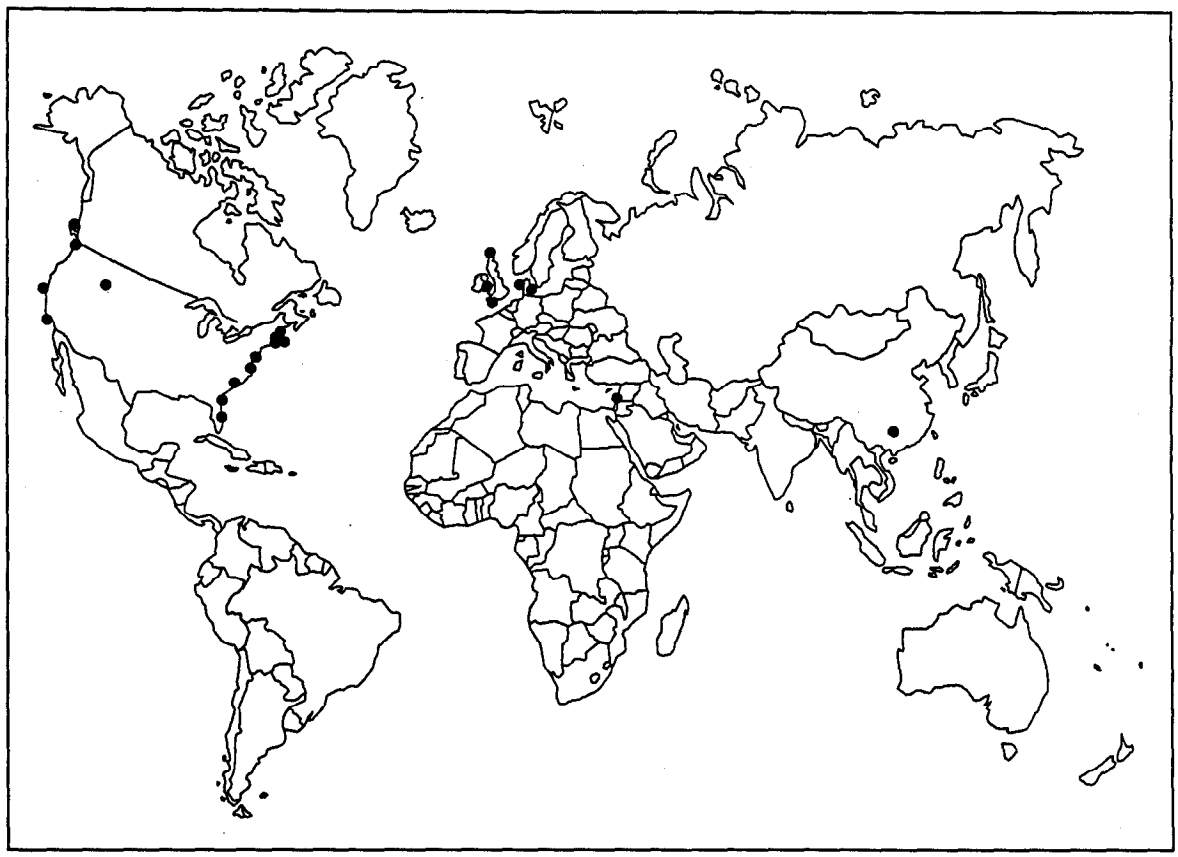

Figure 1. Location of sediment pore water samples reported in the literature

A summary of hydrogen sulfide concentrations reported for sediment pore water is given in Table 1. Because of discrepancies in how concentrations were collected, analyzed, and reported, the term hydrogen sulfide is used to refer to total sulfides (i.e., $H_2S + HS^- + S^=$) throughout this report. Hydrogen sulfide concentrations reported for three freshwater sites (i.e., salinity <1 ppt) ranged from 0 to 293 µM H_2S/ℓ. In estuarine systems (i.e., salinity = 1 to 30 ppt), reported concentrations of hydrogen sulfide were much higher, ranging between 0 and 10,000 µM H_2S/ℓ. At the marine sites (i.e., salinity >30 ppt), reported hydrogen sulfide concentrations ranged from 0 to 79,000 µM H_2S/ℓ. A study by Boulegue, Lord, and Church (1982) reported pore water hydrogen sulfide concentrations (0.1 to 5.06 µM H_2S/ℓ) for a hypersaline site (salinity >35 ppt).

Most documents reported quantitative grain-size classification (e.g., sand, silt, and clay) only. Based on this limited descriptive information, there did not appear to be a relationship between the sediment grain size and elevated levels of hydrogen sulfide.

Eleven of the twenty-five studies reported total organic carbon (TOC). In general, higher concentrations of H_2S were associated with TOC values of 2 to 10 percent, while lower concentrations were associated with TOC values of less than 1 percent (see Table 1).

Many of the studies reviewed reported pore water hydrogen sulfide concentrations as a function of sediment depth. For data reported in this way, there was a trend toward increasing hydrogen sulfide concentration with increasing sediment depth.

Sulfide concentrations have been shown to vary temporally. Seasonally, sulfide concentrations have been shown to fluctuate with allochthonous, organic enrichment and sulfate reduction being lower in winter and higher in the summer and fall (Hines, Knollmeyer, and Tugel 1989; Luther et al. 1986; Bagarinao 1992).

The most commonly used method for pore water collection was by centrifugation (i.e., 19 of 40 samples for which a method was reported). The spectrophotometric method (i.e., colorimetric-methylene blue) was the most frequently used method of analysis (i.e., 23 of 49 samples for which a method was reported).

5 Effects Data

Effects concentrations of hydrogen sulfide in aquatic organisms were obtained from 20 publications for 18 freshwater (i.e., 7 invertebrates and 12 fish) and 14 marine species (i.e., 12 invertebrates and 2 fish). Nearly all of the studies reviewed (19 of 20) examined effects of H_2S using aqueous exposure (i.e., no sediments). Data are summarized in Table 2.

Freshwater invertebrates showed effects on survival, growth, and/or reproduction at concentrations between 0.1 to 30 µM H_2S/ℓ. Reported effects on survival, growth, reproduction, percent normal development, and/or other physiological responses for freshwater fish were found at concentrations between 0.2 and 260 µM H_2S/ℓ.

In general, marine organisms appeared to be more tolerant of H_2S compared with freshwater species. Effects on survival, growth, reproduction, percent normal development, and/or other behavioral/physiological responses in marine invertebrates were found at concentrations between 2.9 and 1,470 µM H_2S/ℓ. Bagarinao and Vetter (1989) reported survival effects concentrations ranging from 525 to 7,000 µM H_2S/ℓ for two species of marine fish with survival as the end point.

6 Discussion

A simple comparison of Table 1 with Table 2 indicates that effects concentrations are on average several orders of magnitude lower than reported environmental pore water concentration of H_2S. In an attempt to quantify this difference, both exposure and effects data were plotted as cumulative probability curves (Figure 2). Effects data were plotted using either the LC50/EC50 concentration or preferentially the LOEC if available. This figure allows a direct comparison of effects and exposure data. The likelihood (i.e., probability) of any particular concentration along these curves can be determined by noting the corresponding "y" value for that concentration. For example, this figure indicates that 90 percent of reported effects occurred at concentrations <100 µM H_2S/ℓ (see arrows intersecting effects curve, Figure 2), while the majority (>55 percent) of the reported environmental exposure concentrations were >100 µM H_2S/ℓ (see arrows intersecting exposure curve, Figure 2). Without further caveats, this would suggest a strong potential for hydrogen sulfide to cause widespread toxicity in many sediments. However, there are a number of potential biases in this limited data set that must be considered prior to reaching such a conclusion.

Because it is difficult to collect and analyze samples for H_2S, it is likely that most of the reported pore water concentrations have been collected from areas where the presence of hydrogen sulfide is strongly suspected. Many of the sediment samples in Table 1 are from organically enriched and at least intermittently anaerobic environments (e.g., marsh sediments). Consequently, the data in Table 1 may tend to overestimate the concentration of pore water H_2S concentrations in aquatic or marine environments and exaggerate the potential risk of toxicity.

Secondly, even if the data in Table 1 and Figure 2 are reflective of naturally occurring concentrations of H_2S, organisms are not continuously exposed to these concentrations. A simplistic comparison of effects and pore water exposure concentrations is somewhat misleading. Only Thompson et al. (1991) reported exposing test organisms to sediments with adjusted pore water concentrations of H_2S. Most of the studies cited in Table 2 considered only aqueous exposures. Fish (freshwater and marine) generally do not come into contact with undiluted pore water. The only time fish may come in contact with H_2S in dredged material toxicity testing is during elutriate tests designed to evaluate the transient water column effects of dredged material disposal.

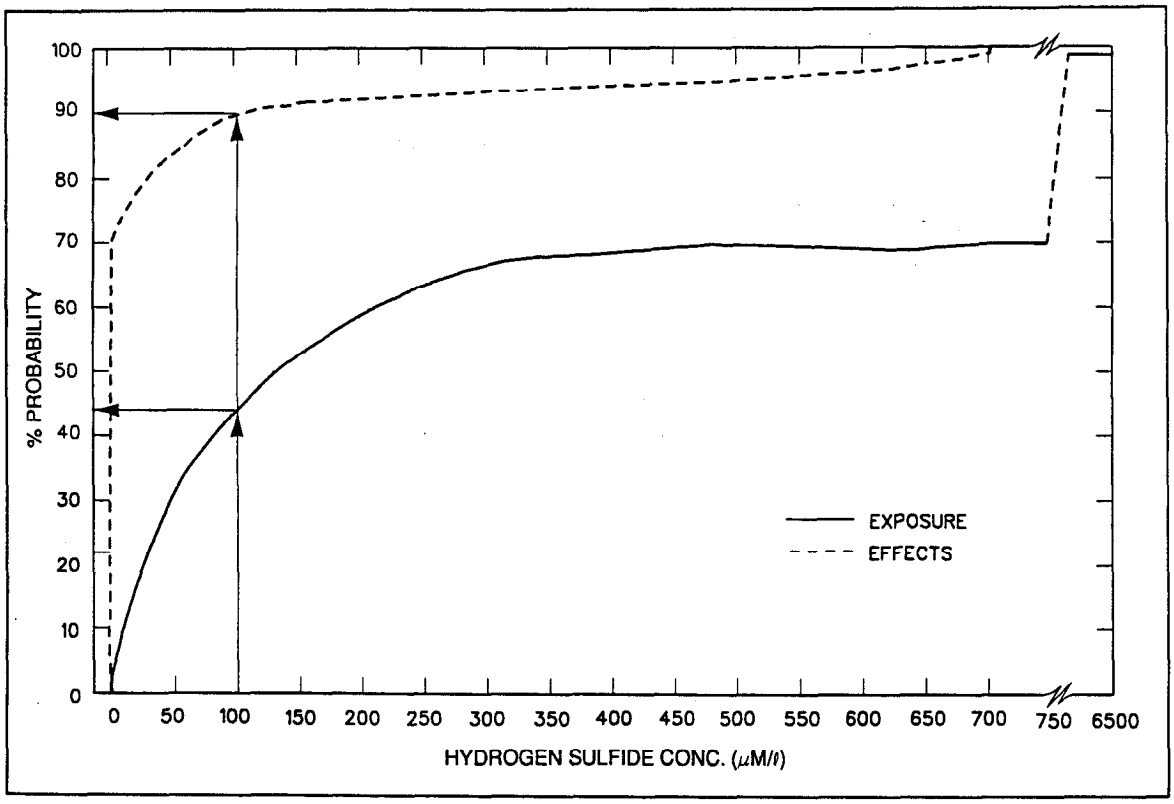

Figure 2. Probability distribution for biological effects concentrations (μM H_2S/ℓ) and environmental sediment pore water exposure concentrations (μM H_2S/ℓ) reported in the literature

During elutriate tests, whole sediment is slurried with dilution water in a 1:4 volume ratio (sediment:water) and allowed to settle; exposures are prepared from the resulting overlying water. Even in these tests, the risk of H_2S toxicity is probably small because of dilution and rapid oxidation of H_2S (since these tests are conducted under oxygenated conditions).

Whole sediment tests are usually conducted with benthic infaunal invertebrates. Many of these animals (e.g., polychaetes and amphipods) are tube builders that circulate oxygenated overlying water through their burrows, substantially reducing or even eliminating exposure to pore water H_2S. In addition to behavioral adaptations, many of these animals have also developed physiological mechanisms to eliminate or detoxify H_2S (for a more complete discussion of sulfide tolerance and other adaptations limiting exposure to H_2S, see Bagarinao 1992).

The sheer diversity of information and lack of comparability among data sets reviewed during this study (i.e., differences in collection, analysis, and reporting of data) make estimating the potential risk of pore water H_2S toxicity in sediment bioassays problematic. To provide a more certain estimate of the potential risk of pore water H_2S toxicity in dredged material bioassays, it would be necessary to begin collecting effects information in a way that reflects probable exposure (i.e., via sediment pore water). Accuracy of

exposure information could be enhanced (i.e., respective of the purpose of this review) through the routine collection and analysis of dredged material pore water for H_2S by the USACE. Until this information becomes available, the assumption must be made on the basis of this review that sediment pore water H_2S represents a potentially significant toxicant in dredged material bioassays.

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Table 1
Sediment Pore Water Concentrations of Hydrogen Sulfide and Related Information Reported in the Literature

Reported H_2S Concentrations (units)	H_2S Concentrations µM/ℓ[1]	Salinity[2]	Grain Size	%TOC	Depth of Collected Sediment cm	Method of Pore Water Collection	Method of H_2S Analysis	Sample Location	Reference
0-0.15 mM	0-150	FW.	N.R.[3]	N.R.	0-10	In-situ diffusion sampler	N.R.	Bath Lake, Yellow Stone National Park, MT	Ward and Olsen 1980
0-10 ppm	0-293	FW.	Silt/ Clay	N.R.	0-5	Centrifuge	Spectro-photometric	Lake Kinneret, Israel	Serruya et al. 1974
<1 µM	<1.0	FW.	Silt	N.R.	0-2	Centrifuge	Spectro-photometric	Lake Brabrand, Denmark	Elsgaard and Jorgensen 1992
0.07-0.5 ppm	2-15	N.R.	N.R.	N.R.	N.R.	Measured in situ	Sulfide selective electrode	Paddy Fields, China	Shu-zheng, Zhi-guang, and Tian-Rren 1982
0-3 mM	0-3,000	EST.	Sand/ Silt	3.73-8.40	0-80	Squeezer	Titration	Loch Dutch, Scotland	Krom and Sholkovitz 1977
0-85 µg/ℓ	0-2.5	EST.	Sand/ Silt	N.R.	0-20	Vacuum sampler	Spectro-photometric	Isle of Mann, UK	McLachlan 1978
50-300 µM/ℓ	50-300	EST.	Sand/ Silt	2.1	0-6	Centrifuge	Spectro-photometric	Kysing Fjord, Denmark	Elsgaard and Jorgensen 1992
0-200 µM	0-200	EST.	Sand/ Silt	N.R.	0-12	Squeezer	Spectro-photometric	Kysing Fjord, Denmark	Fossing and Jorgensen 1990
1 mM	1,000	EST.	Sand/ Silt	8	2-3	Centrifuge	Spectro-photometric	Aarhus Bay, Denmark	Elsgaard and Jorgensen 1992

(Sheet 1 of 6)

[1] To convert from reported units to µM/ℓ, the following conversion factors were used: µM/ml × 1,000; mM × 1,000; µg/ℓ ÷ 34.08; ppm or mg/ℓ × 29.34.
[2] FW. = freshwater (<1 ppt); EST. = estuarine (1 to 30 ppt); MAR. = marine (30 to 35 ppt); HYPER. = hypersaline (>35 ppt).
[3] N.R. = not reported.

Table 1 (Continued)

Reported H_2S Concentrations (units)	H_2S Concentrations µM/ℓ[1]	Salinity[2]	Grain Size	%TOC	Depth of Collected Sediment, cm	Method of Pore Water Collection	Method of H_2S Analysis	Sample Location	Reference
0 µM	0	EST.	N.R.	N.R.	0-12	Squeezer	Spectro-photometric	Aarhus Bay, Denmark	Fossing and Jorgensen 1990
61-88 ppm	1,800-2,600	EST.	Sand/ Clay	2	0-15	N.R.	Ion-selective electrode	BP Horseshoe Bay, Lower Medway Estuary, Kent, U.K.	Wharfe 1977
9.6-70 ppm	280-2,000	EST.	Silt/ Clay	1-10	0-15	N.R.	Ion-selective electrode	E. Rainham, Lower Medway Estuary, Kent, U.K.	Wharfe 1977
7.4-10 ppm	220-290	EST.	Silt/ Clay	1-10	0-15	N.R.	Ion-selective electrode	Bedlams Bottom, Lower Medway Estuary, Kent, U.K.	Wharfe 1977
9.6-43 ppm	280-1,260	EST.	Silt/ Clay	5	0-15	N.R.	Ion-selective electrode	Hoo, Lower Medway Estuary, Kent, U.K.	Wharfe 1977
6.4-34 ppm	190-1,000	EST.	Silt/ Clay	5	0-15	N.R.	Ion-selective electrode	Damhead Creek, Lower Medway Estuary, Kent, U.K.	Wharfe 1977
7.7-10 ppm	225-290	EST.	Silt/ Clay	3	0-15	N.R.	Ion-selective electrode	Motney Hill, Lower Medway Estuary, Kent, U.K.	Wharfe 1977
2.1-10 ppm	60-290	EST.	Silt/ Clay	5	0-15	N.R.	Ion-selective electrode	Lower Upnor, Lower Medway Estuary, Kent, U.K.	Wharfe 1977

(Sheet 2 of 6)

Table 1 (Continued)

Reported H_2S Concentrations (units)	H_2S Concentrations µM/ℓ[1]	Salinity[2]	Grain Size	%TOC	Depth of Collected Sediment, cm	Method of Pore Water Collection	Method of H_2S Analysis	Sample Location	Reference
8.7-10 ppm	255-290	EST.	Silt/ Clay	5	0-15	N.R.	Ion-selective electrode	B.P. Colemouth Creek, Lower Medway Estuary, Kent, U.K.	Wharfe 1977
2.1-7.4 ppm	60-220	EST.	Sand/ Clay	2-3	0-15	N.R.	Ion-selective electrode	Gillingham, Lower Medway Estuary, Kent, U.K.	Wharfe 1977
0-2.8 µM/ml	0-2,800	EST.	Fine Sand/ Silt/ Clay	1.2-10	0-80	Squeezer	Idiometric titration	Limfjorden, Denmark	Jorgensen 1977
0-219 µM	0-219	EST.	Silt	N.R.	0-10	Squeezer	Spectro-photometric	Aarhus Bay, Denmark	Thamdrup et al. 1994
0-10 mM	0-10,000	EST.	N.R.	3.1-4.0	0-140	In situ diffusion sampler	Spectro-photometric	Sannich Inlet, WA	Murray, Grundmanis, and Smethie 1978
100-200 mg/L	3,000-5,900	EST.	Sand/ Silt/ Clay	0.4-0.8	N.R.	Centrifuge	Colormetric (Hach kit)	Sequim Bay, WA	Moore and Dillon 1993
0-2.5 mM	0-2,500	EST.	N.R.	N.R.	0-20	Vacuum-sampler	Spectro-photometric	Chapman's Marsh, NH	Hines, Knollmeyer, and Tugel 1989
0-4 mM	0-4,000	EST.	N.R.	1.7-3.4	0-12	Centrifuge	Spectro-photometric	Chesapeake Bay	Roden and Tuttle 1992, 1993

(Sheet 3 of 6)

Table 1 (Continued)

Reported H_2S Concentrations (units)	H_2S Concentrations $\mu M/\ell$[1]	Salinity[2]	Grain Size	%TOC	Depth of Collected Sediment, cm	Method of Pore Water Collection	Method of H_2S Analysis	Sample Location	Reference
0-3.5 mM	0-3,500	EST.	Silt/ Clay	2-10	0-9	Squeezer	Spectro-photometric	Goat Island, SC	King 1988
0-3 mM	0-3,000	EST.	N.R.	N.R.	0-30	In situ diffusion sampler	Spectro-photometric	Sapelo Island, GA	King et al. 1982
<0.1 ppm	<2.9	EST.	Sand/ Silt/ Clay	0.4-0.6	N.R.	Centrifuge	Colormetric (Hach kit)	Alcatraz environs, San Francisco, CA	Moore and Dillon 1993
<0.1 ppm	<2.9	EST.	Sand/ Silt/ Clay	0.4-0.5	N.R.	Centrifuge	Colormetric (Hach kit)	Alcatraz mound, San Francisco, CA	Moore and Dillon 1993
<0.1 ppm	<2.9	EST.	Silt/ Clay/ Sand	0.2-0.7	N.R.	Centrifuge	Colormetric (Hach kit)	Bay Farm, San Francisco, CA	Moore and Dillon 1993
<0.1 ppm	<2.9	EST.	Sand/ Silt/ Clay	0.03-0.15	N.R.	Centrifuge	Colormetric (Hach kit)	Oakland Inner Harbor, Oakland, CA	Moore and Dillon 1993
<0.1 ppm	<2.9	EST.	Silt/ Sand/ Clay	0.4-1.4	N.R.	Centrifuge	Colormetric (Hach kit)	Oakland Outer Harbor, Oakland, CA	Moore and Dillon 1993
<0.1 ppm	<2.9	EST.	Silt/ Clay/ Sand	0.09-0.34	N.R.	Centrifuge	Colormetric (Hach kit)	Turning Basin, Oakland Harbor, Oakland, CA	Moore and Dillon 1993

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Table 1 (Continued)

Reported H_2S Concentrations (units)	H_2S Concentrations µM/ℓ[1]	Salinity[2]	Grain Size	%TOC	Depth of Collected Sediment, cm	Method of Pore Water Collection	Method of H_2S Analysis	Sample Location	Reference
<0.1 ppm	<2.9	MAR.	Sand/ Silt/ Clay	0.4-0.5	N.R.	Centrifuge	Colormetric (Hach kit)	Point Reyes, San Francisco, CA	Moore and Dillon 1993
0.1-2.0 mM	100-20,000	MAR.	Sandy Peat	N.R.	5-20	Squeezer	Spectro-photometric	Great Sippewisett Marsh, MA	Howarth et al. 1983
1-79 mM	100-79,000	MAR.	N.R.	N.R.	0-20	Squeezer, centrifuge, in situ diffusion sampler	Spectro-photometric	Great Sippewisset Marsh, MA	Howes, Dacey, and Wakeham 1985
0-9 mM	0-9,000	MAR.	Clay/ Sand	2.5-3.5	0-16	Centrifuge	Spectro-photometric	Flax Pond, Long Island, NY	Swider and Mackin 1989
0-300 µm	0-300	MAR.	Silt/ Clay	N.R.	0-150	Squeezer	Spectro-photometric	Long Island Sound, NY	Goldharber et al. 1977
23.6 mg/ℓ	700	MAR.	Silt/ Sand	4.3	0-5	Centrifuge	Spectro-photometric	Palos Verdes Outfall, Los Angeles, CA	Thompson et al. 1989
229 mg/ℓ	6,700	MAR.	Silt/ Sand	2.8	0-5	Centrifuge	Spectro-photometric	Los Angeles 7-mile Outfall, CA	Thompson et al. 1989
0.3 mg/ℓ	9.0	MAR.	Silt/ Sand	6.3	0-5	Centrifuge	Spectro-photometric	Los Angeles Harbor, CA	Thompson et al. 1989
0.6 mg/ℓ	18.0	MAR.	Silt/ Sand	1.1	0-5	Centrifuge	Spectro-photometric	Dana Pt., CA	Thompson et al. 1989

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Table 1 (Concluded)

Reported H_2S Concentrations (units)	H_2S Concentrations µM/ℓ[1]	Salinity[2]	Grain Size	%TOC	Depth of Collected Sediment, cm	Method of Pore Water Collection	Method of H_2S Analysis	Sample Location	Reference
3-8 µM	3.0-8.0	MAR.	N.R.	3.1-4.7	3-11	Centrifuge	High Performance Liquid Chromatography	Santa Barbara Basin, CA	Cary, Vetter, and Felbeck 1989
32.9-166 µM/ℓ	30-170	MAR.	Sand/ Silt	0.11	0.4	Squeezer	Spectro-photometric	Newport Bay, CA	Thompson et al. 1991
32-436 µg/ℓ	1.0-13.0	MAR.	N.R.	N.R.	15-45	Vacuum-sampler	Ion-selective electrode	IRC-12, Indian River Lagoon, FL	Rey et al. 1992
20-137 µg/ℓ	0.6-4.0	MAR.	N.R.	N.R.	15-45	Vacuum-sampler	Ion-selective electrode	Blue Hole, Indian River Lagoon, FL	Rey et al. 1992
0.6-33 µg/ℓ	0.02-1.0	MAR.	N.R.	N.R.	15-45	Vacuum-sampler	Ion-selective electrode	Tidal Creek, Indian River Lagoon, FL	Rey et al. 1992
0.01-8.7 ppm	0.3-255	MAR.	Sand/ Clay	1-2	0-15	N.R.	Ion-selective electrode	Isle of Grain, Lower Medway Estuary, Kent, U.K.	Wharfe 1977
0-9 µM	0-9	MAR.	Sand/ Silt	N.R.	0-14	Squeezer	Spectro-photometric	Skallinger Marsh, Denmark	Thamdrup et al. 1994
0.01-5.06 mM	0.01-5.06	HYPER.	N.R.	N.R.	0-54	Squeezer	Titration/Ion-selective electrode	Great Marsh, DW	Boulegue, Lord, and Church 1982

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Table 2
Effects Concentrations of Hydrogen Sulfide and Other Relevant Information Reported in the Literature for Freshwater and Marine, Invertebrates and Fish

Species	Common Name	Life-Stage/Size	End Point	Duration	LC_{50} or EC_{50}[1] µM/ℓ	NOEC[2] µM/ℓ	LOEC[3] µM/ℓ	Reference
Freshwater Invertebrates								
B. vagans	Mayfly	4-6 mm	Survival	96 hr	0.6	0.05-0.07	N.R.[4]	Oseid and Smith 1974a
E. simulans	Mayfly	13-21 mm	Survival	96 hr	9.0	0.7-1.2	N.R.	Oseid and Smith 1974a
H. limbata	Mayfly	14-35 mm	Survival	96 hr	3.0	0.2-0.4	N.R.	Oseid and Smith 1974a
H. limbata	Mayfly	Nymph	Survival	138 days	N.R.	0.7	1.2	Smith et al. 1976a (USEPA)
Procambarus	Crayfish	Egg	Survival	447 days; 112 days	N.R.	0.2; 0.4	0.4; 0.5	Smith et al. 1976a (USEPA)
Procambarus	Crayfish	Juvenile	Growth	196 days	N.R.	0.2	0.3-0.4	Smith et al. 1976a (USEPA)

(Sheet 1 of 10)

[1] LC_{50} = concentration estimated to result in 50-percent mortality of the test organisms within a given period of time (usually 96 hr); EC_{50} = concentration estimated to produce an effect other than mortality within a given period of time (usually 96 hr).
[2] NOEC = highest concentration for which no significant effects were reported.
[3] LOEC = lowest concentration for which significant effects were reported.
[4] Pore water concentrations.

Table 2 (Continued)

Species	Common Name	Life-Stage/Size	End Point	Duration	LC_{50} or EC_{50}[1] µM/ℓ	NOEC[2] µM/ℓ	LOEC[3] µM/ℓ	Reference
Freshwater Invertebrates (Continued)								
A. militaris	Isopod	5-13 mm	Survival	96 hr	30	2.0-4.0	N.R.	Oseid and Smith 1974a
C. richmondensis laurentianus	Amphipod	6-15 mm	Survival	96 hr	25	2.0-3.0	N.R.	Oseid and Smith 1974a
G. pseudolimnaeus	Amphipod	8-16 mm	Survival	96 hr	2.0	0.1-0.2	N.R.	Oseid and Smith 1974a
G. pseudolimnaeus	Amphipod	N.R.	Survival	96 hr	0.6-0.7	N.R.	N.R.	Oseid and Smith 1974b (TAFS)
G. pseudolimnaeus	Amphipod	N.R.	Survival	65 days - 105 days	N.R.	<0.06	>0.06	Oseid and Smith 1974b (TAFS)
G. pseudolimnaeus	Amphipod	Adult	Survival and Reproduction	65 days - 105 days	N.R.	0.05-0.08	0.1	Smith et al. 1976a (EPA)
Freshwater Fish								
O. mykiss	Rainbow trout	Egg	Survival	96 hr	1.4	N.R.	N.R.	Smith and Oseid 1972
O. mykiss	Rainbow trout	Egg	Survival	96 hr	0.6	N.R.	N.R.	Smith et al. 1976a (USEPA)

Table 2 (Continued)

Species	Common Name	Life-Stage/Size	End Point	Duration	LC_{50} or EC_{50}[1] µM/ℓ	NOEC[2] µM/ℓ	LOEC[3] µM/ℓ	Reference
Freshwater Fish (Continued)								
O. mykiss	Rainbow trout	Egg	Survival and Growth	145 days; 111 days	N.R.	0.1; 0.2	0.2; 0.5	Smith et al. 1976a (USEPA)
O. mykiss	Rainbow trout	Sac fry	Survival and Growth	100 days	N.R.	0.1	0.3	Smith et al. 1976a (USEPA)
O. mykiss	Rainbow trout	Fry	Survival	96 hr	0.6	N.R.	N.R.	Smith and Oseid 1972
O. mykiss	Rainbow trout	Fry	Survival	96 hr	0.2	N.R.	N.R.	Smith et al. 1976a (USEPA)
O. mykiss	Rainbow trout	Fry; 10 days	Survival and Growth	90 days	N.R.	0.1	0.2	Smith et al. 1976a (USEPA)
O. mykiss	Rainbow trout	Juvenile	Survival	96 hr	0.5	N.R.	N.R.	Smith et al. 1976a (USEPA)
O. mykiss	Rainbow trout	Juvenile; 50 days	Survival and Growth	50 days	N.R.	0.2	0.4	Smith et al. 1976a (USEPA)
O. mykiss	Rainbow trout	N.R.	Survival	8 hr	N.R.	N.R.	12	Ortiz et al. 1993
S. trutta	Brown trout	Fry	Survival	96 hr	0.2	N.R.	N.R.	Reynolds and Haines 1980
S. fontinalis	Brook trout	Fry	Survival	96 hr	0.6	N.R.	N.R.	Smith et al. 1976a (USEPA)

Table 2 (Continued)

Species	Common Name	Life-Stage/Size	End Point	Duration	LC_{50} or EC_{50}[1] µM/ℓ	NOEC[2] µM/ℓ	LOEC[3] µM/ℓ	Reference
Freshwater Fish (Continued)								
S. fontinalis	Brook trout	Swim-up fry	Survival	96 hr	0.9	N.R.	N.R.	Smith et al. 1976a (USEPA)
S. fontinalis	Brook trout	Juvenile	Survival	96 hr	0.7-1.0	N.R.	N.R.	Smith et al. 1976a (USEPA)
S. fontinalis	Brook trout	Juvenile	Growth	72 days; 120 days	N.R.	0.3	0.4	Smith et al. 1976a (USEPA)
S. fontinalis	Brook trout	Adult	Reproduction	45-75 days	N.R.	<0.2	0.2	Smith et al. 1976a (USEPA)
S. vitreum	Walleye	Egg	Survival	96 hr	1.5-2.5	N.R.	N.R.	Smith and Oseid 1972
S. vitreum	Walleye	Egg	% normal development	19 days - 20 days	N.R.	0.7	1.1	Smith and Oseid 1972
S. vitreum	Walleye	Fry	Survival	96 hr	0.2	N.R.	N.R.	Smith and Oseid 1972
S. vitreum	Walleye	Juvenile	Survival	234 days; 225 days	N.R.	0.1; 0.2	0.2; 0.5	Smith et al. 1976a (USEPA)
E. Lucius	Northern pike	Egg	Survival	96 hr	1.0	0.4	0.5	Adelman and Smith 1970
E. lucius	Northern pike	Egg	Survival	96 hr	1.0-1.1	N.R.	N.R.	Smith and Oseid 1972

Table 2 (Continued)

Species	Common Name	Life-Stage/Size	End Point	Duration	LC_{50} or EC_{50}[1] µM/ℓ	NOEC[2] µM/ℓ	LOEC[3] µM/ℓ	Reference
Freshwater Fish (Continued)								
E. Lucius	Northern pike	Sac fry	Survival	96 hr	0.8	0.1	0.2	Adelman and Smith 1970
L. macrochirus	Bluegill	Egg	Growth and Survival	316 days; 120 days	N.R.	N.R.	0.05; 0.09	Smith et al. 1976a (USEPA)
L. macrochirus	Bluegill	Fry; 30 mm	Survival	3 hr	114	53	60	Bonn and Follis 1967
L. macrochirus	Bluegill	Juvenile	Growth, Survival, and Reproduction	826 days	N.R.	0.06	0.13	Smith et al. 1976a (USEPA)
L. macrochirus	Bluegill	Adult	Growth and Reproduction	288 days; 200 days	N.R.	0.1; 0.2	0.3; 0.4	Smith et al. 1976a (USEPA)
L. macrochirus	Bluegill	Egg	Survival	96 hr	0.6	N.R.	N.R.	Smith et al. 1976b (TAFS)
L. macrochirus	Bluegill	Fry; 0.3-0.8 cm	Survival	96 hr	0.4-1.2	N.R.	N.R.	Smith et al. 1976b (TAFS)
L. macrochirus	Bluegill	Juvenile; 3.9-4.3 cm	Survival	96 hr	1.4	N.R.	N.R.	Smith et al. 1976b (TAFS)
L. macrochirus	Bluegill	Adult; 12 cm	Survival	96 hr	1.3	N.R.	N.R.	Smith et al. 1976b (TAFS)

Table 2 (Continued)

Species	Common Name	Life-Stage/Size	End Point	Duration	LC_{50} or EC_{50}[1] µM/ℓ	NOEC[2] µM/ℓ	LOEC[3] µM/ℓ	Reference
Freshwater Fish (Continued)								
P. promelas	Fathead minnow	Egg	Survival	96 hr	1.6	N.R.	N.R.	Smith, Oseid, and Olson 1976b (ES&T)
P. promelas	Fathead minnow	Egg	Survival, Growth, and Reproduction	37 days - 345 days	N.R.	0.03	0.1	Smith, Oseid, and Olson 1976b (ES&T)
P. promelas	Fathead minnow	Sac fry	Survival, Growth, and Reproduction	297 days	N.R.	0.1	0.3	Smith et al. 1976a (USEPA)
P. promelas	Fathead minnow	Fry; 5.6-5.9 mm	Survival	96 hr	0.3	N.R.	N.R.	Smith, Oseid, and Olson 1976b (ES&T)
P. promelas	Fathead minnow	Juvenile	Survival	96 hr	0.6-1.5	N.R.	N.R.	Smith, Oseid, and Olson 1976b (ES&T)
P. promelas	Fathead minnow	Juvenile	Survival and Growth	112 days	N.R.	0.2	0.4	Smith et al. 1976a (USEPA)
C. auratus	Goldfish	Egg	Growth	430 days	N.R.	0.3	0.4	Smith et al. 1976a (USEPA)
C. auratus	Goldfish	Juvenile	Growth	294 days	N.R.	0.4	1.0	Smith et al. 1976a (USEPA)

Table 2 (Continued)

Species	Common Name	Life-Stage/Size	End Point	Duration	LC_{50} or EC_{50}[1] µM/ℓ	NOEC[2] µM/ℓ	LOEC[3] µM/ℓ	Reference
Freshwater Fish (Continued)								
C. auratus	Goldfish	Adult	Reproduction	294 days	N.R.	0.2	0.4	Smith et al. 1976a (USEPA)
C. carpio	Carp	50-60 g; 13-15 cm (female)	Gonado-somatic index; Hepato-somatic index	30 days	N.R.	N.R.	260	Kumar and Mukherjee 1988
C. commersoni	Common sucker	Egg	Survival	96 hr	0.8	N.R.	N.R.	Smith and Oseid 1972
C. commersoni	Common sucker	Fry	Survival	96 hr	0.4-0.8	N.R.	N.R.	Smith and Oseid 1972
C. commersoni	Common sucker	Egg	% normal development	19-20 days	N.R.	0.5	0.9	Smith and Oseid 1972
I. punctatus	Channel catfish	Fry; 30 mm	Survival	3 hr	53.0-230.0	44	62	Bonn and Follis 1967
Marine Invertebrates								
L. pictus	Urchin	Adult; 14-23 mm	Survival	96 hr	2.9	N.R.	1.4	Thompson et al. 1991
L. pictus	Urchin	Adult; 14-23 mm	Behavior-Avoidance	49 days	N.R.	33.0[5]	92.0[5]	Thompson et al. 1991

Table 2 (Continued)

Species	Common Name	Life-Stage/Size	End Point	Duration	LC_{50} or EC_{50}[1] µM/ℓ	NOEC[2] µM/ℓ	LOEC[3] µM/ℓ	Reference
Marine Invertebrates (Continued)								
L. pictus	Urchin	Adult; 14-23 mm	Survival	49 days	N.R.	33.0[5]	92.0[5]	Thompson et al. 1991
L. pictus	Urchin	Adult; 14-23 mm	Growth	49 days	N.R.	<33.0[5]	33.0[5]	Thompson et al. 1991
L. pictus	Urchin	Adult; 14-23 mm	Male gonad weight	49 days	N.R.	<33.0[5]	33.0[5]	Thompson et al. 1991
S. purpurtus	Urchin	Embryo	% normal development	48 hr	5.9	3.0	4.0	Knezovich et al. 1994 (SETAC)
M. edulis	Mussel	30-50 mm	Survival	96 hr	>1,470.0	N.R.	N.R.	Abel 1976
M. edulis	Mussel	30-50 mm	Respiratory rate	96 hr	60	N.R.	N.R.	Abel 1976
M. edulis	Mussel	Embryo	% normal development	48 hr	3.0	1.7	2.8	Knezovich et al. 1994 (SETAC)
A. islandica	Clam	N.R.	Total glycogen-phosphorylase activity	10 days	N.R.	N.R.	200	Oeschger and Storey 1993
N. arenaceodentata	Polychaete	2-3 wks post-emergence	Survival	96 hr	N.R.	150	590	Dillon, Moore, and Gibson 1993

Table 2 (Continued)

Species	Common Name	Life-Stage/Size	End Point	Duration	LC_{50} or EC_{50}[1] µM/ℓ	NOEC[2] µM/ℓ	LOEC[3] µM/ℓ	Reference
Marine Invertebrates (Continued)								
N. virens	Polychaete	0.65 g	Respiratory rate	N.A.	N.R.	50	100	Miron and Kristensen 1993
N. diversicolor	Polychaete	0.65 g	Respiratory rest period	N.A.	N.R.	1,000	1,200	Miron and Kristensen 1993
N. succinea	Polychaete	0.65 g	Respiratory rate	N.A.	N.R.	50	100	Miron and Kristensen 1993
C. capitata Sp. I	Polychaete	Larvae	Settlement time	3 hr	N.R.	N.R.	500	Dubilier 1988
S. benedicti	Polychaete	Adult	Survival	50 hr	N.R.	N.R.	>20	Miron and Kristensen 1993
E. estuarius	Amphipod	Adult	Survival	48 hr	104	N.R.	60	Knezovich et al. 1994 (SETAC)
R. abronius	Amphipod	Adult	Survival	48 hr	50	N.R.	46	Knezovich et al. 1994 (SETAC)

Table 2 (Concluded)

Species	Common Name	Life-Stage/Size	End Point	Duration	LC_{50} or EC_{50}[1] µM/ℓ	NOEC[2] µM/ℓ	LOEC[3] µM/ℓ	Reference
Marine Fish								
G. mirabalis	Long-jawed mudsucker	4-5 g	Survival	96 hr	525	N.R.	N.R.	Bagarinao and Vetter 1989
F. parvipinnus	Killifish	3-8 g	Survival	96 hr	700	N.R.	N.R.	Bagarinao and Vetter 1989

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13. ABSTRACT ***(Maximum 200 words)***

Generally, hydrogen sulfide is not treated as a contaminant of concern in the regulatory evaluation of dredged material since it undergoes rapid oxidation and dilution during dredging and disposal. However, because dredged material is evaluated using effects-based testing (i.e., whole sediment and elutriate toxicity tests), there is the potential for H_2S to exert toxicity and confound the regulatory decision-making process. To evaluate the potential for hydrogen sulfide toxicity in dredged material bioassays, a literature review and survey to U.S. Army Corps of Engineers Divisions and Districts were conducted. Data included (a) reported environmental pore water exposure concentrations of hydrogen sulfide and (b) effects concentrations shown to cause toxicity in laboratory studies with aquatic species. While the majority (>60 percent) of reported environmental pore water concentrations were >100 mM H2S/L, almost all (90 percent) of reported effects were found at concentrations <100 μM H_2S/L. This simple comparison of reported exposure and effects concentrations suggests that there is a strong potential for hydrogen sulfide toxicity in dredged material bioassays. However, a number of biases in this limited data set are discussed that must be considered before any definitive conclusions can be drawn.

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