

Toxicity of Ammonia in Aquatic Sediments and its Implications for Sediment Quality Evaluation and Management

Anne Jones-Lee, Ph.D. and G. Fred Lee, Ph.D., P.E., D.E.E.

G. Fred Lee & Associates

El Macro, California

June, 1993

ABSTRACT

Ammonia is a common contaminant in many aquatic sediments which can arise from both natural and anthropogenic sources. Un-ionized ammonia is highly toxic to many forms of aquatic life. Studies on a variety of US waterway sediments taken near municipal industrial areas show that ammonia is a frequent cause of toxicity in laboratory toxicity tests of aquatic sediments. Sediment quality investigations should evaluate whether sediment toxicity is caused by ammonia in the sediments and its significance to the beneficial uses of the waterbody.

KEY WORDS - ammonia, toxicity, sediments

INTRODUCTION

Jones and Lee (1978) and Lee *et al.* (1978) found that sediments from many US waterways showed some toxicity to test organisms in four-day laboratory toxicity tests on sediment elutriates. The toxicity, however, was far less than would be predicted based on the concentrations of the variety of contaminants in the sediments (Jones *et al.*, 1981). Jones and Lee (1988) subsequently reported that for a group of those sediments they examined further, the toxicity appeared to be due to the ammonia in the sediments. Ankley *et al.* (1990) also reported that ammonia was the constituent responsible for toxicity found in laboratory tests of sediments from the upper Fox River in Wisconsin.

AMMONIA IN AQUATIC SEDIMENTS

While the aquatic chemistry of organics, heavy metals, and many other chemicals in aquatic sediments is complex, the chemistry of ammonia is relatively simple and straightforward, especially in marine systems. Ammonia exists in aquatic sediments in two forms, the ammonium ion (NH_4^+) and un-ionized ammonia (NH_3). Un-ionized ammonia is highly toxic to some forms of aquatic life, while the ammonium ion is largely non-toxic or significantly less toxic. The distribution of ammonia between those two forms in water is controlled by pH, temperature, and ionic strength. In freshwater sediments at pH 8.0 and 27°C, about 3% of the total ammonia is present in the un-ionized form, while in saline water (20) of the same temperature and pH, about 4% of the total ammonia is in the un-ionized form (US EPA, 1989; Thurston *et al.*, 1979).

The US EPA (1989) has determined that the chronic water quality criterion for un-ionized ammonia in marine waters is 0.035 mg/L NH₃ based on the sensitivity of mysids, various types of shrimp, and fish. The US EPA (1989) determined a saltwater Final Acute Value for ammonia of 0.465 mg NH₃/L. In their studies of the toxicity of ammonia from New York Harbor sediments to *Palaemonetes pugio* (grass shrimp) Jones and Lee (1988) found that the concentrations of un-ionized ammonia in those systems in which the 96-hr survival was about 50% was on the order of 0.3 to 0.5 mg N/L. That finding was in keeping with those reported by Hanson (1986) and Hall *et al.* (1978). Such an LC50, however, was considerably lower than that reported by US EPA (1989) for another investigator's tests with juvenile and adult grass shrimp, of 2.6 mg/L. That value is believed to be in error.

For freshwater, the US EPA (1987) has established an un-ionized ammonia four-day average chronic criterion of about 0.02 mg/L NH₃; at lower temperatures and pH's, that value is about 0.01 mg/L NH₃. Acute:chronic ratios range from 3 to 43 mg/L NH₃; 96-hr LC50's were reported as low as 0.08 mg/L NH₃. Salmonids are among the most ammonia-sensitive of the freshwater organisms tested.

In marine sediments, ammonia would be expected to show little tendency to sorb onto sediments because of the high ionic concentrations of sodium, calcium, and magnesium in the interstitial waters, the comparatively low concentration of ammonia, and the low sorption tendency of ammonia compared with calcium, magnesium, and sodium. Ammonia associated with the sediment would thus be present largely dissolved in the interstitial water.

Many of the analytical procedures used for measuring ammonia in sediments involve the addition of water (e.g., ammonia electrode measurements). It is therefore necessary to consider any dilution of interstitial water ammonia associated with the chemical analytical or toxicity test procedures used. The measurement of ammonia in sediments is sometimes accomplished after distillation of the ammonia from the sediment sample. Under these conditions, the amount of water added in the distillation flask does not affect the results of the test.

In order to compute the un-ionized ammonia concentration in the interstitial water for the ambient sediments, it is necessary to know the percent moisture in the sediments. Typically, aquatic sediments range from 40% to 60% moisture. A marine sediment interstitial water with 40% solids, pH 8.0, temperature 20°C and total ammonia of 1.5 mg N/Kg dry weight, would be expected to have sufficient un-ionized ammonia in the interstitial waters to exceed the US EPA chronic water quality criterion for ammonia.

In the 1970's, the authors (Lee *et al.*, 1978 and Jones and Lee, 1978) conducted an extensive study of sediment-associated contaminants largely in estuarine and marine waterways near urban and industrial centers throughout the US. Concentrations of ammonia and a variety of other contaminants (including heavy metals, chlorinated hydrocarbon pesticides, and PCB's) were determined, and aquatic life toxicity evaluated. As shown in Table 1, the total ammonia concentration in the 34 sediments

they reported, principally from waterways on the East, Gulf, and West coasts, ranged from 19 to 670 mg N/Kg dry wt.; the mean concentration was 194 mg N/Kg dry weight with a standard deviation of 172. It is therefore clear that the ammonia concentration in the interstitial waters of those sediments, which are thought to be representative of many of the coastal water sediments near urban and industrial centers of the US, greatly exceed the US EPA water quality criterion and would therefore be expected to be toxic to some forms of aquatic life.

Table 1. Concentrations of Ammonia in Sediment from Studies of Lee *et al.* (1978)

Location	Sediment Ammonia (mg N/kg dry wt.)
Oakland, CA	30
Los Angeles, CA (site 1)	624
Newport, RI	24
Stamford, CT	123
Norwalk, CT (site 1)	173
Norwalk, CT (site 2)	168
Foundry Cove, NY	114
Menominee River, MI/WI (site 1)	670
Menominee River, MI/WI (site 2)	382
Wilmington, DE	47
WES Lake, MS	66
Apalachicola, FL (site 1)	178
Apalachicola, FL (site 2)	82
Apalachicola, FL (site 3)	158
Apalachicola, FL (site 4)	146
Apalachicola, FL (site 5)	168
Upper Mississippi River, MN	25
James River, VA	294
Bailey Creek, VA	131
Texas City Channel, TX (site 4)	294
Texas City Channel, TX (site 5)	36
Texas City Channel, TX (site 6)	222

Houston Ship Channel, TX (site 1)	182
Houston Ship Channel, TX (site 2)	218
Houston Ship Channel, TX (site 3)	83
Port LaVaca, TX	19
Duwamish River, WA (site 1)	33
Duwamish River, WA (site 2)	131
Duwamish River, WA (site 3)	90
Perth Amboy Channel, NJ	628
Perth Amboy Anchorage, NJ	274
Bay Ridge Channel, NY	235
Mobil Bay, AL (site 1)	381
Mobil Bay, AL (site 2)	197

Mean 194

S.D. 172

TEST ORGANISMS AND CONDITIONS FOR MEASURING SEDIMENT TOXICITY

In *"Evaluation of Dredged Material Proposed for Ocean Disposal Testing Manual,"* US EPA and US ACE (1991) allow the use of a variety of test organisms for evaluating sediment toxicity. It is of interest to examine the sensitivity of those organisms to ammonia and how the toxicity tests are conducted with reference to the dilution of interstitial water by the addition of test water.

The standard elutriate toxicity test (US EPA and US ACE, 1991) prescribes the mixing of one volume sediment (which is often 40 to 60% water) with four volumes of water. The concentration of ammonia in the interstitial water is thus diluted about 1:9. It is therefore possible that a sediment could be toxic to ambient organisms but not be found to be toxic under the conditions of the test because of the dilution that has occurred in conducting the test. This could be especially true for chemicals like ammonia which, as discussed above, would be expected to be present in interstitial marine and calcareous freshwater waters and not desorbed from the sediment solids. Not considered in the test conditions, however, is the dilution that would occur in ambient waters.

While some aquatic organisms are highly sensitive to the toxic effects of ammonia, others are remarkably insensitive. Some of the organisms that are being widely used today to test for sediment toxicity, such as the amphipods, are remarkably insensitive to ammonia. Ogle (1993) has reported that the amphipod *Rhepoxynius abronius* shows an ammonia toxicity of about 10 to 20 times less than many other "sensitive" test organisms commonly used for toxicity tests. While the issue of ammonia toxicity to amphipods such as *Rhepoxynius abronius* appears to have been overlooked, it is now becoming clear that amphipods may not be good test organisms for sediment toxicity because of their insensitivity to ammonia relative to that of fish, mysids, and shrimp. Greater consideration needs to be given to the selection of appropriate benthic and epibenthic test organisms to generate useful, interpretable laboratory toxicity test data.

As discussed by Lee and Jones (1987, 1991, 1992) and Jones and Lee (1988), a high priority needs to be given to translating the results of laboratory toxicity tests to impacts on beneficial uses of the ambient water; this is especially true for sediment-associated contaminants. Sediments from many natural water systems can be shown to have readily measurable toxicity in a laboratory test system while the ambient waters support good fisheries and other aquatic life resources. The demonstration of statistically significant toxicity in laboratory tests cannot be presumed to indicate that ecologically significant toxicity or impairment of designated beneficial uses occurs in the ambient water, or indeed that any toxic effects occur in the ambient water. The finding of toxicity in laboratory tests is not tantamount to impairment of beneficial uses of waterbodies that should, *a priori*, cause the public and private interests to pay millions to billions of dollars in an effort to remove the manifestation of toxicity in laboratory tests.

CONTROL OF SEDIMENT AMMONIA

Since the ammonia associated with sediments is of potential concern for toxicity to aquatic life in the interstitial waters and at the sediment-water interface, it is important to understand how ammonia becomes associated with sediments. The aqueous environmental chemistry of ammonia reveals that it does not precipitate and does not tend to sorb onto sediments to a significant extent under typical environmental conditions of ionic strength and relative distribution of major cations in solution. A possible exception to this situation can occur in non-calcareous low TDS waters. Therefore, unlike many other toxic chemicals of potential concern, ammonia does not become part of the sediments through direct sorption or precipitation reactions. Ammonia becomes part of sediments through settling of particulate organic nitrogen. The organic nitrogen, in turn, is mineralized through bacteria-mediated ammonification reactions which lead to a build-up of total ammonia in the interstitial waters.

The concentration of ammonia that develops in sediments is controlled by the rates of ammonification and transport of ammonia from the interstitial water to the overlying water. In sediments that have a low oxygen demand, especially in the upper few

millimeters to a centimeter or so, nitrification reactions can convert some of the interstitial water ammonia to nitrite and nitrate. However, since most sediments are anoxic, and since nitrification does not occur under anoxic conditions, the transport of ammonia from the sediments to the overlying waters is the primary mechanism for limiting the ammonia build-up in sediments. As discussed by Lee (1970) and Lee and Jones (1987), the transfer of materials from interstitial water to the overlying water is controlled by physical mixing - advective - processes and not by concentration-gradient - diffusional - processes.

In some areas, particulate organic nitrogen in sediments is derived from untreated wastewater. This was found, for example, in New York Harbor, which until a few years ago received the discharge of large amounts of untreated, raw domestic sewage through direct discharge as well as in combined sewer overflows (Jones and Lee, 1988). For most sediments, particulate organic nitrogen is derived from plant protein sources in non-point source terrestrial runoff and from the decomposition of autochthonous aquatic plants especially phytoplankton.

In order to address the control of ammonia in sediments, it is necessary to determine whether the ammonia that is in the sediments is, in fact, adversely affecting beneficial uses of the ambient waters. If it is determined to be causing a significant adverse impact, it is necessary to understand and quantify the sources of particulate organic nitrogen for the sediments. The relative roles of terrestrial point sources and non-point sources and of aquatic plant sources of particulate organic N in contributing to the ammonia in the sediments that cause aquatic life toxicity need to be determined. Once the significant sources have been identified, a determination needs to be made of the extent to which the controllable sources can be controlled and the impact that that control would have on the ammonia toxicity of the sediments and the aquatic life resources of concern to the public, which must ultimately pay for such control.

Sufficient understanding of this topic exists to know that in most instances point-source discharges are not the primary source of organic N leading to ammonia toxicity in sediments. In the opinion of the authors, there are few US municipal and industrial wastewater discharges that contribute sufficient concentrations of particulate organic N to be a significant source of ammonia in aquatic sediments. This situation has a significant impact on control options and programs that might be considered for any given sediment.

Given the dominant sources of ammonia in sediments (Lee and Jones, 1992), it is evident that controlling ammonia toxicity in sediments will not be readily achieved in most instances. The ubiquitous sources of particulate organic nitrogen, many of which are natural, will make controlling sediment toxicity due to ammonia difficult and very expensive. If it is not possible to control the ammonia toxicity in a sediment, then appropriate questions should be raised about controlling other contaminants that may be toxic to aquatic life in the sediments. There seems to be little justification for spending large amounts of public money to control the manifestation of laboratory toxicity to *Rhepoxynius abronius* caused by a heavy metal or a non-polar organic

such as a chlorinated hydrocarbon pesticide or a PAH, while ignoring the ammonia toxicity exhibited by another group of organisms that is of even greater importance to the public. These issues will become extremely important as efforts are made to try to implement the sediment quality criteria and standards development approaches being advocated by the US EPA and some states into control programs for point-source and non-point source discharges and runoff.

DISCUSSION AND CONCLUSIONS

There is sufficient ammonia in the sediments (interstitial water) of many US waterways, especially marine and calcareous freshwater systems, to be of potential concern for aquatic life toxicity. While there is a widespread potential for aquatic life toxicity due to sediment-associated ammonia, the water quality significance of that ammonia and of the toxicity manifested from those sediments in laboratory tests is not understood. It is also apparent that some of the test organisms thought to be very sensitive for evaluating sediment toxicity, such as some amphipods, are not suitably sensitive to ammonia to reliably evaluate potential toxicity due to sediment-associated ammonia.

There is need to gain a much better understanding of the potential benefits of controlling sediment toxicity manifested in laboratory toxicity tests. There is also need to develop approaches to more reliably identify those sediments which, owing to their chemical contamination, should be "remediated" and have contaminant input discharge control in order to protect designated beneficial uses of the waterbodies in which they lie.

While the focus of this paper is the potential significance of sediment-associated ammonia as a cause of aquatic life toxicity, similar issues exist for H₂S and low DO conditions in sediments. Sediments that have sufficient ammonia to cause toxicity to important aquatic organisms could have sufficient H₂S and sufficiently low DO to themselves cause toxicity to aquatic life. Latimer (1992) reported that only a small part of the sediment toxicity found in the US EPA EMAP studies of sediments in the nearshore marine waters of the eastern US was caused by Priority Pollutants. Low DO, as well as ammonia and hydrogen sulfide, would be expected to contribute to the toxicity found in those sediments. The US EPA did not include measurement of ammonia in sediments in the initial EMAP studies.

As more toxicity identification evaluation work is done on the causes of aquatic life toxicity in laboratory tests of sediments, there are increasing reports of the importance of ammonia. In a study of copper toxicity Burgess *et al.* (1993) reported that the toxicity found was likely due to ammonia. The San Francisco Bay Regional Water Quality Control Board (SFBRWQCB, 1993) reported the finding of toxicity in a "pristine" reference site; that toxicity could readily have been caused by ammonia.

The finding of ammonia, H₂S and low dissolved oxygen as a common cause of sediment toxicity raises important questions about regulating sediment quality using

equilibrium partitioning based sediment quality criteria. Lee and Jones-Lee (1993a) have discussed the importance of any investigation of sediment toxicity, including evaluation of the presence and significance of toxicity due to ammonia, H₂S, and low dissolved oxygen conditions. Failure to consider the importance of these constituents in sediments in influencing sediment toxicity - sediment quality could result in inappropriate assessment of the benefits of sediment remediation that focuses on heavy metals, organics, or other constituents. Such an approach could result in the sediments still being toxic to key forms of aquatic life due to ammonia, hydrogen sulfide or low dissolved oxygen after remediation has occurred for heavy metals and other constituents.

Some regulatory agencies, including the US EPA in its National Sediment Inventory, are using co-occurrence based chemical sediment "quality" values as part of a sediment regulatory program (US EPA, 1994). Long and Morgan ER-L and ER-M values (Long and Morgan, 1990) and the MacDonald PEL values (MacDonald, 1992) attempt to correlate total chemical concentrations for selected chemical constituents and a sediment toxic response for sediments taken from a wide variety of locations in the US. The tabulation of the co-occurring value of toxic response and chemical concentrations is used to claim that whenever a chemical concentration above a value that someone claims to have found toxicity irrespective of its cause, is justification to assert that any sediment with a concentration above this value could have toxicity due to that chemical. However, in developing these values the developers chose to ignore the ammonia, hydrogen sulfide, and low dissolved oxygen data that was in the data bases that they used. Such an approach is not technically valid for several reasons. As discussed herein, most of the sediment toxicity is due to these chemicals. Further, it has been known for over 20 years that there is no relationship between the toxicity of sediments and the total concentrations of chemicals in the sediments (Lee and Jones, 1992, Lee and Jones-Lee, 1993a). Daskalakis and O'Connor (1994) have reported that based on an evaluation of the US EPA EMAP data for sediments along the eastern US that the Long and Morgan ER-M values did not reliably predict sediment toxicity as measured by toxicity tests using an amphipod.

The so-called toxic responses that were found by various investigators in the Long and Morgan and MacDonald data bases were due to a significant extent to ammonia, H₂S and low DO. As discussed by Lee and Jones-Lee (1994), co-occurrence based values tend to significantly overestimate the water quality significance of the chemicals considered and ignore the vast array of non-regulated chemicals and non-considered chemicals. Any sediment quality ranking - evaluation system must consider the potential significance of ammonia, hydrogen sulfide, and low dissolved oxygen if it is to have any technical validity.

REFERENCES

Ankley, G., Katko, A., and Arthur, J. (1990). Identification of ammonia as an important sediment-associated toxicant in the lower Fox River and Green Bay, Wisconsin. *Environ. Tox. & Chem.* 9:312-322.

Ankley, G., Mattson, V., Leonard, E., West, C., and Bennett, J. (1993). Predicting the acute toxicity of copper in freshwater sediments: Evaluation of the role of acid-volatile sulfide. *Environ. Tox. & Chem.* 12:315-320.

Burgess, R., Schweitzer, K., McKinney, R., and Phelps, D. (1993). Contaminated marine sediments: Water column and interstitial toxic effects. *Environ. Tox. & Chem.* 12:127-138.

Daskalakis, K. D., O'Connor, T. P. (1994). Inventory of chemical concentrations in coastal and estuarine sediments. NOAA Technical Memorandum NOS ORCA 76.

Hall, L., Buikema, A., and Cairns, J. (1978). The effects of a simulated refinery effluent on the grass shrimp, *Palaemonetes pugio*. *Archives of Environmental Contaminant Toxicology* 7:23-35.

Hanson, D. (1986). US EPA Narragansett Laboratory. Personal communication to G. Fred Lee.

Jones, R. A., and Lee, G. F. (1978). Evaluation of the elutriate test as a method of predicting contaminant release during open water disposal of dredged sediment and environmental impact of open water dredged material disposal, Vol. I: Discussion. Technical Report D78-45, US Army Corps of Engineers, WES, Vicksburg, MS, 217 pp., August.

Jones, R. A., and Lee, G. F. (1988). Toxicity of US waterway sediments with particular reference to the New York Harbor area. In: Chemical and Biological Characterization of Sludges, Sediments, Dredge Spoils and Drilling Muds, ASTM STP 976 pp. 403-17 ASTM Philadelphia, PA.

Jones, R. A., Mariani, G., and Lee, G. F. (1981). Evaluation of the significance of sediment-associated contaminants to water quality. In: Utilizing Scientific Information in Environmental Quality Planning, Proc. AWRA Symposium AWRA, Minneapolis, MN, pp. 34-45.

Latimer, R. (1992). The extent and severity of sediment contamination in the estuaries of the mid-Atlantic region. Presented at US EPA Forum on the Extent and Severity of Sediment Contamination, Chicago, IL, April.

Lee, G. F. (1970). Factors affecting the transfer of materials between water and sediments. University of Wisconsin Eutrophication Information Program, Literature Review No. 1, 50 pp.

Lee, G. F., and Jones, R. A. (1987). Water quality significance of contaminants associated with sediments: An overview. In: Fate and Effects of Sediment-Bound Chemicals in Aquatic Sediments, Pergamon Press, Elmsford, NY, pp. 1-34.

Lee, G. F., and Jones, R. A. (1991). Comments on 'Workplan for the Development of Sediment Quality Objectives for Enclosed Bays and Estuaries of California.' Submitted to D. Maughan, Chairman, California Water Resources Control Board, Sacramento, CA, May.

Lee, G. F., and Jones, R. A. (1992). Sediment quality criteria development: Technical difficulties with current approaches, and suggested alternatives. Report of G. Fred Lee & Associates, El Macero, CA, January. Condensed version published In: Proc. HMCRI R&D 92 Conference on the Control of Hazardous Materials, HMCRI, Greenbelt, MD, pp. 204-211.

Lee, G. F., and Jones, R. A. (1992). Sediment quality criteria development: Technical difficulties with current approaches, and suggested alternatives. Report of G. Fred Lee & Associates, El Macero, CA, January. Condensed version published In: Proc. HMCRI R&D 92 Conference on the Control of Hazardous Materials, HMCRI, Greenbelt, MD, pp. 204-211.

Lee, G. F., and Jones-Lee, A. (1993a). Sediment quality criteria: Numeric chemical- vs. biological effects-based approaches. Proceedings of Water Environment Federation National Conference, Surface Water Quality & Ecology, Anaheim, CA, pp. 389-400.

Lee, G. F., and Jones-Lee, A. (1993b). Equilibrium partitioning-based values: Are they reliable for screening contaminated sediment? Letter to the editor of Environ. Sci. & Technol. 27:7pp.

Lee, G. F., and Jones-Lee, A. (1994). "Co-Occurrence" in sediment quality assessment. Submitted for publication, Water Environment Federation, Water Environment & Technology.

Lee, G. F., Jones, R., Saleh, F., Mariani, G., Homes, D., Butler, J., and Bandyopadhyay, P. (1978). Evaluation of the elutriate test as a method of predicting contaminant release during open water disposal of dredged sediment and environmental impact of open water dredged material disposal, Vol II: Data Report. Technical Report D78-45, US Army Corps of Engineers WES, Vicksburg, MS, 1186 pp., August.

Long, E., and Morgan, L. (1990). The potential for biological effects of sediment-sorbed contaminants tested in the national status and trends program. NOAA Technical Memorandum NOS OMA 52, NOAA, Seattle, WA, March.

MacDonald, D. (1992). Development of an approach to the assessment of sediment quality in Florida coastal waters. Submitted to Florida Department of Environmental Regulation, May.

Ogle, S. (1993) Presentation at NorCal SETAC annual meeting, May.

SFBRWQCB (1993). Reissuance of draft waste discharge requirements for: US Army Corps of Engineers, San Francisco District calendar years 1993 through 1994 maintenance dredging and disposal site management. San Francisco Bay Regional Water Quality Control Board Order 93-. February 17.

Thurston, R., Russo, R., and Emerson, K. (1979). Aqueous Ammonia Equilibrium - Tabulation of Percent Un-ionized Ammonia, US EPA 600/3-79-091, Environmental Research Laboratory, Duluth, MN, August.

US ACE (US Army Corps of Engineers) (1989). Technical review comments on the apparent effects threshold (AET). Report to US EPA Science Advisory Board from Waterways Experiment Station, Vicksburg, MS, February.

US EPA (1987). Quality Criteria for Water 1986. US EPA 44/5-86-001, Office of Water Regulations and Standards, Washington, DC, May.

US EPA (1989b). Ambient water quality criteria for ammonia (saltwater)-1989. EPA 440/5-88-004, Office of Water Regulations and Standards, Criteria and Standards Division, Washington, DC, April.

US EPA (1994) "Proceedings of the national sediment inventory workshop" US Environmental Protection Agency Office of Water, Washington, DC.

US EPA and US ACE (US Army Corps of Engineers) (1991). Evaluation of dredged material proposed for ocean disposal - testing manual. EPA-503/8-91/001, February.

Reference as: "Jones-Lee, A. and Lee, G. F., 'Potential Significance of Ammonia as a Toxicant in Aquatic Sediments,' Proc. First International Specialized Conference on Contaminated Aquatic Sediments: Historical Records, Environmental Impact, and Remediation, International Assoc. Water Quality, Milwaukee, WI, pp. 223-232, June (1993)."