Stormwater Runoff Water Quality Newsletter
Devoted to Urban/Rural Stormwater Runoff
Water Quality Management Issues

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Editor: Anne Jones-Lee, PhD
Contributor to This Issue:
G. Fred Lee, PhD, PE, BCEE

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This issue of the Newsletter provides information on recent discussions of **nanotechnology and nanomaterials** and their implication for environmental quality. It also updates discussions in several previous Newsletters on **LEHR/Putah Creek Mercury issues**, **water quality modeling**, **regulating agriculture runoff**, and **sediment quality evaluation with respect to sediment quality objectives and impact of nutrients on sediment toxicity**, and the **occurrence of Hg and PCBs in California lake and reservoir fish.**

NANOTECHNOLOGY

March 19, 2009 Symposium

The California Department of Toxic Substances Control (DTSC) and the University of California Toxic Substances Research and Teaching Program held a one-day symposium on March 19, 2009 devoted to regulation of nanomaterials. The DTSC website
[http://www.dtsc.ca.gov/TechnologyDevelopment/Nanotechnology/index.cfm]
provides information on this symposium as well as other background information on nanotechnology and potential environmental issues.

As described on the DTSC website,
"*Nanotechnology is the design, characterization, production, and application of structures, devices, and systems by controlling the shape and size at the nanometer scale. Understanding and controlling matter at the nanoscale interests researchers in the sciences, medicine, agriculture, and industry because a material's properties at the nanoscale can be very different from those at a larger scale." "The unique physical, chemical, and biological properties of materials at the nanoscale enable novel applications and functions with the potential to promote enormous societal and economic benefits. Some current innovative applications of nanotechnology include the use of nanomaterials in liquid filtration and water purification, as catalysts in petroleum refining and catalytic converters, and in nanoscale biological imaging. In the near future of two to five years, nanotechnology will be integrated into advanced drug delivery systems, real-time medical diagnostic tools, sensors for airborne chemicals or other toxins, and photovoltaics (solar cells), fuel cells and portable power to provide inexpensive, clean energy.*"

An overview of presentations made at the March 19 symposium is presented below.

Shelia Davis, Executive Director Silicon Valley Toxic Coalition discussed, "*Regulating Emerging Technologies in Silicon Valley and Beyond*" and noted the lack of information on the extent of use, and potential impacts of nanomaterials. She discussed concern over public health and environmental impacts associated with this technology in light of the unanticipated pollution

of groundwater in the Silicon Valley with chlorinated solvents that accompanied the electronics industry there.

Mary Beth Miller, Director, EHS and Facilities Management, Unidym, Inc. discussed, "*The Business of Nanotechnology*." From her familiarity with the development and use of nanomaterials, she addressed the need to address environmental and public health issues associated with these materials. With more than 600 nano companies involved in making more than 1000 products that use nanomaterials, and with several new nanomaterials' being developed each week, the current market is on the order of $2-trillion. However, almost no information is available concerning the public health and environmental aspects and impacts of these materials. This is of great concern since some uses of nanomaterials result in their dispersal in the environment through wastewater discharges, stormwater runoff, landfill emissions, and discharges to the atmosphere. In particular, she noted a need to develop a framework for developing public health and environmental quality information on nanomaterials, information on risk analysis including risk assessment and risk management, and comprehensive life cycle information on the nanomaterials. She also discussed the lack of analytical methods and testing protocols for assessing the potential environmental and public health impacts of nanomaterials, noting that conventional impact assessment approaches such toxicity testing are not likely to be reliable for evaluating the potential impacts of these materials.

Mark Bunger, Research Director, Lux Research, Inc. discussed, "*Nanomaterials in Industry and International Context*." Lux Research develops information, from a business perspective, on materials, including nanomaterials. He noted that while the development of nanomaterials is a world-wide issue, and there are many different types and applications of nanomaterials, there has been little or no consideration given to potential environment and public health impacts.

Timothy Mallory, Professor, School of Law, University of California Los Angeles addressed, "*Modern Regulation and Nanotechnology Innovation*." He discussed the importance of regulating without preventing innovation. He also discussed factors that companies use to consider environmental protection and public health issues associated with its products.

Mike Feuer, California Assembly member, author of AB 1879 which overall gave CalEPA greater authority to regulate toxins in consumer products. Among other things, it requires DTSC to establish a process for identifying and prioritizing chemicals of concern, prepare a multimedia life cycle evaluation, and adopt regulations to establish a process for evaluating how best to limit exposure to, or reduce the hazards of exposure to, chemicals of concern in products. The language of these regulations is available online at http://info.sen.ca.gov/pub/07-08/bill/asm/ab_1851-1900/ab_1879_bill_20080929_chaptered.pdf
Feuer argued that nanomaterials have incredible potential for beneficial uses but that their development and use for the benefit of society must be balanced with adequate regulation of their use and disposal. Issues of concern he noted included the impacts on the health of workers, and of those in the sphere of influence of releases from a manufacturing facilities, as well as sites of use and the disposal of residuals and products containing nanomaterials. He reviewed issues of developing nanomaterial legislation by the state legislature.

Dr. Richard Denison, Senior Scientist of the Environmental Defense discussed "*Nanotechnology Regulation in Washington and Brussels: TSCA vs REACH.*" He pointed out that TSCA has limited authority to review the environmental health and safety of nanomaterials. US EPA has adopted this limited authority to review nanomaterials. REACH is a European regulatory approach for nanomaterials; it is a comprehensive evaluation of potential impacts. He supports making major changes to enable TSCA to undertake more appropriate review of all chemicals including nanomaterials.

Kristan Markey, US EPA Nanomaterials Stewardship Program, discussed, "*EPA Progress and Emerging Regulatory Role of Industrial Nanoscale Materials*." He reviewed the current approach that the US EPA is following in addressing nanomaterials impacts. The US EPA is working to improve the review of nanomaterials through a voluntary approach.

Dr. M.V. Hoek, Associate Professor of Civil and Environmental Engineering at UCLA presented, "*Establishing the New Science of Nano-Safety: Toward Safe Implementation of Nanotechnology.*" He reviewed studies on nanotechnology development being conducted at UCLA, and pointed out that when nanomaterials are introduced into the environment, their surface characteristics change due to sorption and other reactions, which can increase their adverse impacts on human health and aquatic life. University of California Los Angeles and Santa Barbara have developed the Center for Environmental Implementation of Nanotechnology that is becoming active in conducting research on impacts of nanomaterials in the environment.

To subscribe to the DTSC: Nanotechnology listserv or other listservs, please go to http://www.calepa.ca.gov/Listservs/dtsc/.

American Chemical Society Spring 2009 Meeting

The Spring 2009 Annual Meeting of the American Chemical Society (ACS) included presentations devoted to nanotechnology and nanomaterials. In all, more than 30 presentations (audio and slides) on nanomaterials at that meeting have been posted on the ACS website [www.acs.org]. (At the ACS website, click on "Meetings." On the right side of the screen is a box entitled, "Nanoscience, Challenges for the Future;" click on that box to get to the **237th ACS National Meeting Session List** page, then scroll down to view a listing of the presentations available. Click on the one of interest, scroll down, and click the "view" button to view the archived webcast of that presentation.) The direct link to the **237th ACS National Meeting Session List** page is http://www.softconference.com/acschem/. The online content is available for free to anyone.

UPDATES:

Putah Creek and UCD/DOE LEHR Superfund Site –
Mercury in Stormwater Runoff Issues

Stormwater Runoff Water Quality Newsletter NL 11-11 [can be found online at http://www.gfredlee.com/newsindex.htm] included a set of PowerPoint slides and companion discussion of water quality problems in Putah Creek caused by excessive concentrations of mercury, and the role of stormwater runoff from the University of California/ Department of Energy (UCD/DOE) LEHR Superfund site in contributing to the excessive mercury in Putah

Creek fish. That presentation has been developed into a professional paper that has been published as,

> Lee, G. F., and Jones-Lee, A, "LEHR Superfund Stormwater Runoff and Putah Creek Mercury Issues," *Journal Remediation*, **19(2)**:123-134, Spring (2009).
> http://www.gfredlee.com/SJR-Delta/LEHRrunoffHgRemediation.pdf

As discussed in that paper, elevated levels of mercury exist in the surface soils of the LEHR Superfund site, as well as those of other areas of UCD and likely the city of Davis soils. That mercury was likely deposited during periods when Putah Creek waters flooded the area prior to the construction of the upstream Lake Berryessa. Those waters contained elevated levels of mercury from former mercury mines located in the Coast Range upstream of Lake Berryessa.

Because of the elevated levels of mercury in the soils at the LEHR site and the potential runoff of that mercury to Putah Creek and its fish, and in accord with the California Central Valley Regional Water Quality Control Board order, UCD is attempting to control the mercury in runoff from the LEHR site to meet the California Toxics Rule (CTR) mercury criterion of 50 ng/L by placing straw rolls in the path of the stormwater runoff. Visual inspection of the runoff from the LEHR site during stormwater runoff events revealed that the straw rolls were not effective in preventing turbid discharges to Putah Creek that could be transporting mercury from the site to the creek. However, even achieving that CTR criterion will not prevent the stormwater from the LEHR site and other areas from continuing to contribute to the excessive bioaccumulation of mercury in Putah Creek fish. To achieve that goal, mercury concentrations in stormwater runoff would have to be reduced to less than about 5 ng/L.

As discussed by Lee (2009) much more effective monitoring of stormwater runoff LEHR site needs to be conducted to properly evaluate the impacts of that stormwater runoff on water quality in Putah Creek. Such monitoring would also need to focus on determining and evaluating management practices that would, in fact, control mercury in LEHR site stormwater runoff so that it does not continue to contribute to excessive bioaccumulation of mercury in Putah Creek fish.

> Lee, G. F., "Comments on UCD/DOE LEHR Superfund Stormwater Runoff Water Quality Monitoring Program," Report of G. Fred Lee & Associates, El Macero, CA, March (2009).
> http://www.gfredlee.com/DSCSOC/2009/LEHRStormwaterMonComments.pdf

Excessive Bioaccumulation of Mercury and PCBs in California Lake Fish

According to a press release, the California "*State Water Resources Control Board's Surface Water Ambient Monitoring Program (SWAMP) has released the first findings from the largest survey ever conducted in California of contaminants in sport fish from lakes and reservoirs. The results are from the first year of the two year, statewide survey. The results indicate that problems exist in some areas of the state. Mercury and polychlorinated biphenyls (PCBs) are the two greatest concerns. Mercury contamination is largely a legacy of California mining, and can also reach lakes through the air. It is a persistent problem throughout much of the state. Twenty-six percent of the lakes surveyed had at least one fish species with an average mercury level that exceeds the Office of Environmental Health Hazard Assessment (OEHHA) threshold for considering a consumption limit. OEHHA cannot develop new recommendations based solely on data from this study.*

PCBs were second to methylmercury as a potential health concern to consumers of fish caught from California lakes. Approximately thirty-six percent of the lakes had a fish species that exceeded OEHHA's Fish Contaminant Goal. However, only 1 percent of the lakes sampled had a species with an average concentration level that exceeds OEHHA's threshold for considering a recommendation of no consumption. PCBs are persistent chemicals that are now banned in electrical, industrial and other applications. Other pollutants were also found, but generally at low levels.

The Lakes Survey focuses on more than 200 of the most popular fishing lakes in the state. Random sampling of an additional 50 of California's other 9,000 lakes is included to provide the basis for a statistical statewide assessment. The report presents results from monitoring in 2007. In that year, the study team collected over 6,000 fish from 150 lakes and reservoirs. The team sampled another 130 lakes in 2008. Results from this second round, and a more in depth analysis of possible trends, will be available in a final report early 2010. The Lakes Study, Year 1 report evaluating 2007 data is available on the SWAMP website at: http://www.waterboards.ca.gov/water_issues/programs/swamp/lakes_study.shtml."

Modeling Water Quality Impacts of Stormwater Runoff

Newsletter NL 10-9 [can be found online at http://www.gfredlee.com/newsindex.htm] discussed issues of appropriate water quality modeling for assessing water quality impacts of potential pollutants in urban and rural area stormwater runoff. That Newsletter was prompted by the fact that many of what are called stormwater runoff water quality models do not adequately or reliably address water quality issues, i.e., the impairment of the beneficial uses of waterbodies that receive stormwater runoff. As noted in that newsletter, typically used stormwater runoff "water quality models" are actually hydrologic models that track the movement of water during a runoff event. They do not include the aquatic chemistry/toxicology/biology aspects necessary for defining and describing the transport, transformation, availability, and exposure/effects aspects that determine the potential impacts of runoff-associated chemicals on aquatic life-related water quality. In order to properly model stormwater runoff water quality impacts it is necessary to incorporate aquatic chemistry of the potential pollutants in the models.

At the request of the editor of *Civil Engineering News* we prepared a condensed version of the discussion in that Newsletter; it was published as,

> Jones-Lee, A. and Lee, G. F., "Modeling Water Quality Impacts of Stormwater Runoff – Why Hydrologic Models Aren't Sufficient," CENews.com Feature Article, January 29 (2008). http://www.cenews.com/article.asp?id=2631
> http://www.gfredlee.com/Runoff/CENewsStmWaterModeling.pdf

The editor of a new book on water quality modeling requested that that the Jones-Lee and Lee discussion be included in that book; it was recently published:

> Jones-Lee, A., and Lee, G. F., "Modelling Water Quality Impacts of Stormwater Runoff: Why Hydrologic Models Are Insufficient," Chapter 4 IN: **Modelling of Pollutants in Complex Environmental Systems**, Volume I, ILM Publications, St. Albans, Hertfordshire, UK, pp.83-95 (2009).
> http://www.gfredlee.com/Runoff/HydrologicModelsInadeq.pdf

US EPA AQUATOX (Release 3)

AQUATOX is a US EPA simulation model for aquatic systems designed to predict the fate of various pollutants and their effects on the ecosystem. The US EPA website [http://www.epa.gov/waterscience/models/aquatox] provides background information on the development of that model, and access to Release 2.2 of the model.

In June 2008 the draft "AQUATOX Release 3" was released.

> US EPA, "Aquatox (Release 3) Modeling Environmental Fate and Ecological Effects in Aquatic Ecosystems, Draft, June 2008 Volume X: Technical Documentation" US EPA Office of Water (4305) EPA-xxxxxxxxxxx Environmental Protection Agency, DRAFT, JUNE (2008).

The current drafts of the model, technical documentation, and user manual can be downloaded from: http://www.warrenpinnacle.com/prof/AQUATOX/howcani1.html

As described in the draft Technical Documentation,

"The AQUATOX model is a general ecological risk assessment model that represents the combined environmental fate and effects of conventional pollutants, such as nutrients and sediments, and toxic chemicals in aquatic ecosystems."

"The fate portion of the model, which is applicable especially to organic toxicants, includes: partitioning among organisms, suspended and sedimented detritus, suspended and sedimented inorganic sediments, and water; volatilization; hydrolysis; photolysis; ionization; and microbial degradation. The effects portion of the model includes: sublethal and lethal toxicity to the various organisms modeled; and indirect effects such as release of grazing and predation pressure, increase in detritus and recycling of nutrients from killed organisms, dissolved oxygen sag due to increased decomposition, and loss of food base for animals."

Discussion of Water Quality Modeling Issues

Lee and Jones-Lee recently developed the following discussion of issues that need to be considered in using water quality models in regulatory programs:

> Lee, G. F., and Jones-Lee, A., "Reliability of Deterministic Models for Predicting Water Quality Impacts of Alterations in Pollutant Loads," Report of G. Fred Lee & Associates, El Macero, CA, March (2009).
> http://www.gfredlee.com/SurfaceWQ/DeterministicModels.pdf

Update of Regulating Agricultural Runoff Water Quality Impacts

Newsletter 12-1/2 was devoted to issues that should be considered in regulating the water quality impacts of potential pollutants in agricultural runoff/discharges. Lee and Jones-Lee have expanded that discussion to address additional issues associated with evaluating sediment quality impacts. Their updated report is available as:

> Lee, G. F., and Jones-Lee, A., "Issues in Regulating Water Quality Impacts from Irrigated Agricultural Runoff and Discharges in the Central Valley of California," Report of G. Fred Lee & Associates, El Macero, CA, February 4 (2009).
> http://www.gfredlee.com/SurfaceWQ/Impacts-Ag-Runoff.pdf

While the focus of that Newsletter and report was agricultural runoff, much of the discussion of regulatory issues apply to urban and highway stormwater runoff as well. As discussed the approach adopted by the California State Water Resources Control Board (SWRCB) for developing Sediment Quality Objectives (SQOs) is not valid for identifying sediments that are

impaired because the SQOs rely in part on the total concentrations of selected chemicals in the sediments. The total concentration of a chemical or of groups of chemicals in the sediment is not reliably related to the potential for a sediment to cause adverse impact on beneficial uses of the water or sediment. Their inclusion in a screening, assessment, or management protocol serves to skew, in an indefinable manner, the outcome of the assessment – skewing that can result in over-regulation or under-regulation of sediments. It is the toxic/available forms of sediment-associated chemicals in aquatic systems that should be incorporated in sediment quality evaluation. Further many of the approaches suggested in the Sediment Quality Objectives for evaluation of the chemical(s) responsible for sediment toxicity are unreliable for this purpose. The comments developed by Lee and Jones-Lee on technical aspects of the SWRCB SQOs are presented in,

> Lee, G. F., and Jones-Lee, A., "Comments on 'Draft Staff Report, Water Quality Control Plan for Enclosed Bays and Estuaries – Part 1. Sediment Quality Developed by State Water Resources Control Board, California Environmental Protection Agency July 18, 2008'" and Answers to SWRCB Staff Responses to Comments on September 2007 Proposed SQO Development Approach. Submitted to State Water Resources Control Board, Sacramento, CA. Report of G. Fred Lee & Associates, El Macero, CA, September 5 (2008). http://www.gfredlee.com/Sediment/SQOCommentsAnswers.pdf

Another significant problem with the SWRCB SQO approach is their failure to include proper consideration of the impact of nutrients in stimulating the growth of algae that die, settle to the sediments and become a source of oxygen demand that leads to rapid acting inorganic oxygen demand when the sediments are stirred into the water column such as during storms. Newsletter 10-4, 10-5, and 10-6 discuss these issues. They are available at,
http://www.gfredlee.com/newsindex.htm and in,

> Lee, G. F. and Jones-Lee, A., "Role of Aquatic Plant Nutrients in Causing Sediment Oxygen Demand Part I – Origin of Rapid Sediment Oxygen Demand," Report of G. Fred Lee & Associates, El Macero, CA, May (2007).
> http://www.gfredlee.com/Sediment/NutrientSOD1RapidOD.pdf
>
> Lee, G. F., and Jones-Lee, A., "Role of Aquatic Plant Nutrients in Causing Sediment Oxygen Demand Part II – Sediment Oxygen Demand," Report of G. Fred Lee & Associates, El Macero, CA, June (2007).
> http://www.gfredlee.com/Sediment/NutrientSOD2SOD.pdf
>
> Lee, G. F., and Jones-Lee, A., "Role of Aquatic Plant Nutrients in Causing Sediment Oxygen Demand Part III – Sediment Toxicity," Report of G. Fred Lee & Associates, El Macero, CA, June (2007). http://www.gfredlee.com/Sediment/NutrientSOD3Tox.pdf

Figures 1, 2 and 3 at the end of the Newsletter show the processes and importance of considering the role of aquatic plant nutrients in causing sediment toxicity.

The key message is that dischargers and the public could be forced to spend large amounts of money for sediment "remediation" to remove a particular chemical(s) from sediments or to otherwise "remediate" sediments targeted on the basis of an unreliable SQO development approach. Furthermore, sediments that contain sufficient oxygen demand that when stirred into

the water column to cause high levels of aquatic life toxicity, could be left unaddressed because that parameter is not addressed by the SQOs. The Lee and Jones-Lee reports referenced above provide information on the importance and implications of this issue and recommend approaches to address it.

SWRCB NonPoint Source Website

The SWRCB Nonpoint Source (NPS) Implementation Program has developed an extensive website covering both State and Regional Water Board regulatory solutions for reducing polluted runoff in the state. The URL for that new NPS Regulatory Solutions web page is:
http://www.waterboards.ca.gov/water_issues/programs/nps/reg_solutions.shtml.
For more information on the state's NPS Implementation Program, for preventing and reducing polluted runoff, visit the NPS program website at:
http://www.waterboards.ca.gov/water_issues/programs/nps/.

SETAC Pellston Workshops

Beginning in the late 1970s a group of individuals associated with chemical companies, the US EPA, and several universities, including Dr. G. Fred Lee, organized a series of workshops devoted to developing procedures to screen new or expanded-use chemicals for potential environmental impact. Those workshops typically consisted of about 10 to 15 individuals who met for a week at the University of Michigan Biological Station located near Pellston, Michigan to discuss and develop a report on a chosen aspect of assessing environmental impact of chemicals. Through this effort what became known then as the "hazard assessment approach" for screening new and expanded use chemicals for aquatic environmental impact evolved. That approach involves the integrated use of aquatic toxicology/impact and expected environmental concentration/exposure to estimate potential aquatic environmental impact. Subsequently, the Society for Toxicology and Chemistry (SETAC) has organized many workshops on issues of aquatic environmental impact. Background information and a listing of the workshops is available at http://www.setac.org/node/104. At the website http://www.setac.org/node/265, SETAC has made available at no cost, the abstracts of several recent SETAC "Pellston" workshops devoted to:

- Ecological Assessment of Selenium in the Aquatic Environment,
  Science-Based Guidance and Framework for the Evaluation and Identification of PBTs and POPs (persistent, bioaccumulative, and toxic substances (PBTs) and persistent organic pollutants (POPs),
- Evaluation of Persistence and Long-Range Transport of Organic Chemicals in the Environment,
- A Multi-Stakeholder Framework for Ecological Risk Management,
- Use of Sediment Quality Guidelines and Related Tools for the Assessment of Contaminated Sediments Executive Summary Booklet,
- Summary of a SETAC Technical Workshop Porewater Toxicity Testing: Biological, Chemical, and Ecological Considerations with a Review of Methods and Applications, and Recommendations for Future Areas of Research.

The proceedings of these and earlier Pellston workshops provide in-depth discussion of aquatic environmental pollution issues pertinent to evaluating and regulating the water quality impact of chemicals in stormwater runoff and in other sources of potential pollutants.

Figure 1

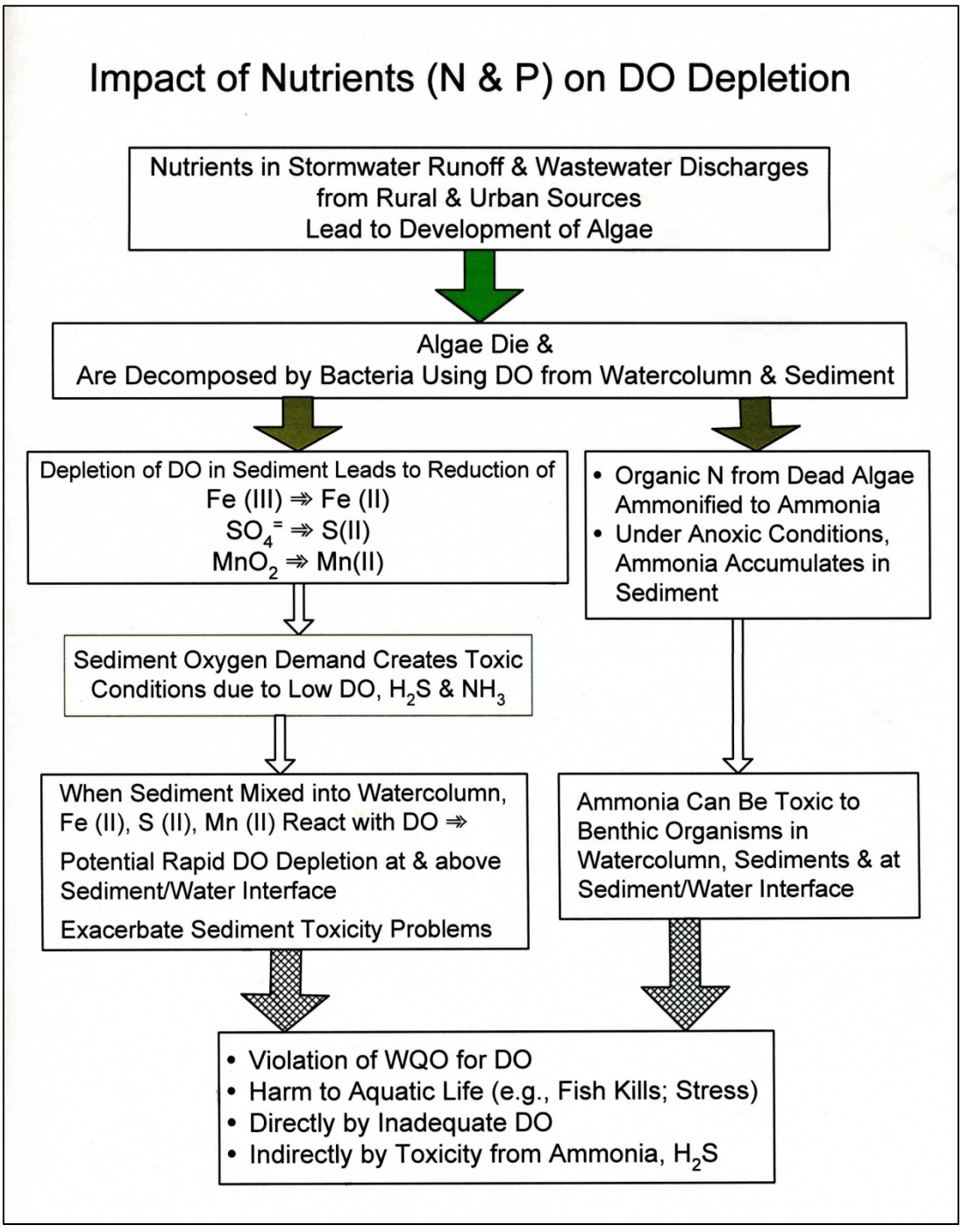

Impact of Nutrients (N & P) on DO Depletion
Nutrients in Stormwater Runoff & Wastewater Discharges from Rural & Urban Sources Lead to Development of Algae
Algae Die & Are Decomposed by Bacteria Using DO from Watercolumn & Sediment
Depletion of DO in Sediment Leads to Reduction of
Fe (III) ⇛ Fe (II)
$SO_4^=$ ⇛ S(II)
MnO_2 ⇛ Mn(II)
• Organic N from Dead Algae Ammonified to Ammonia
• Under Anoxic Conditions, Ammonia Accumulates in Sediment
Sediment Oxygen Demand Creates Toxic Conditions due to Low DO, H_2S & NH_3
When Sediment Mixed into Watercolumn, Fe (II), S (II), Mn (II) React with DO ⇛
Potential Rapid DO Depletion at & above Sediment/Water Interface
Exacerbate Sediment Toxicity Problems
Ammonia Can Be Toxic to Benthic Organisms in Watercolumn, Sediments & at Sediment/Water Interface
• Violation of WQO for DO
• Harm to Aquatic Life (e.g., Fish Kills; Stress)
• Directly by Inadequate DO
• Indirectly by Toxicity from Ammonia, H_2S

Figure 2

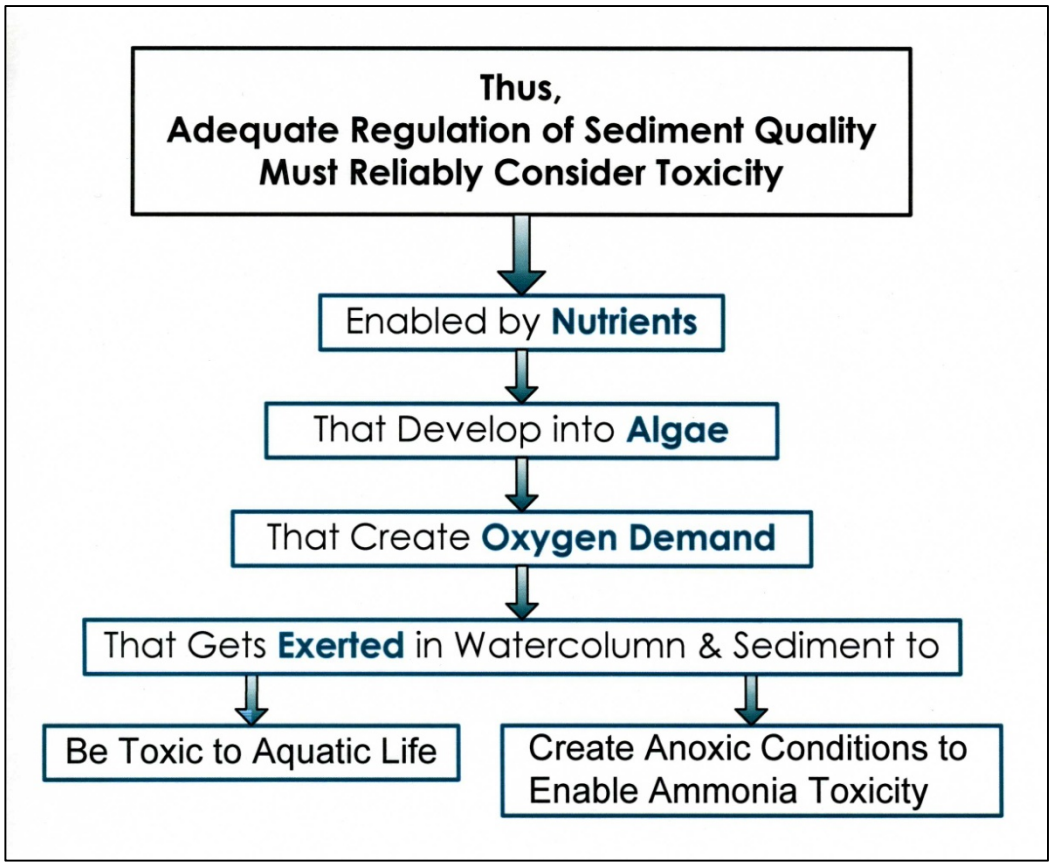
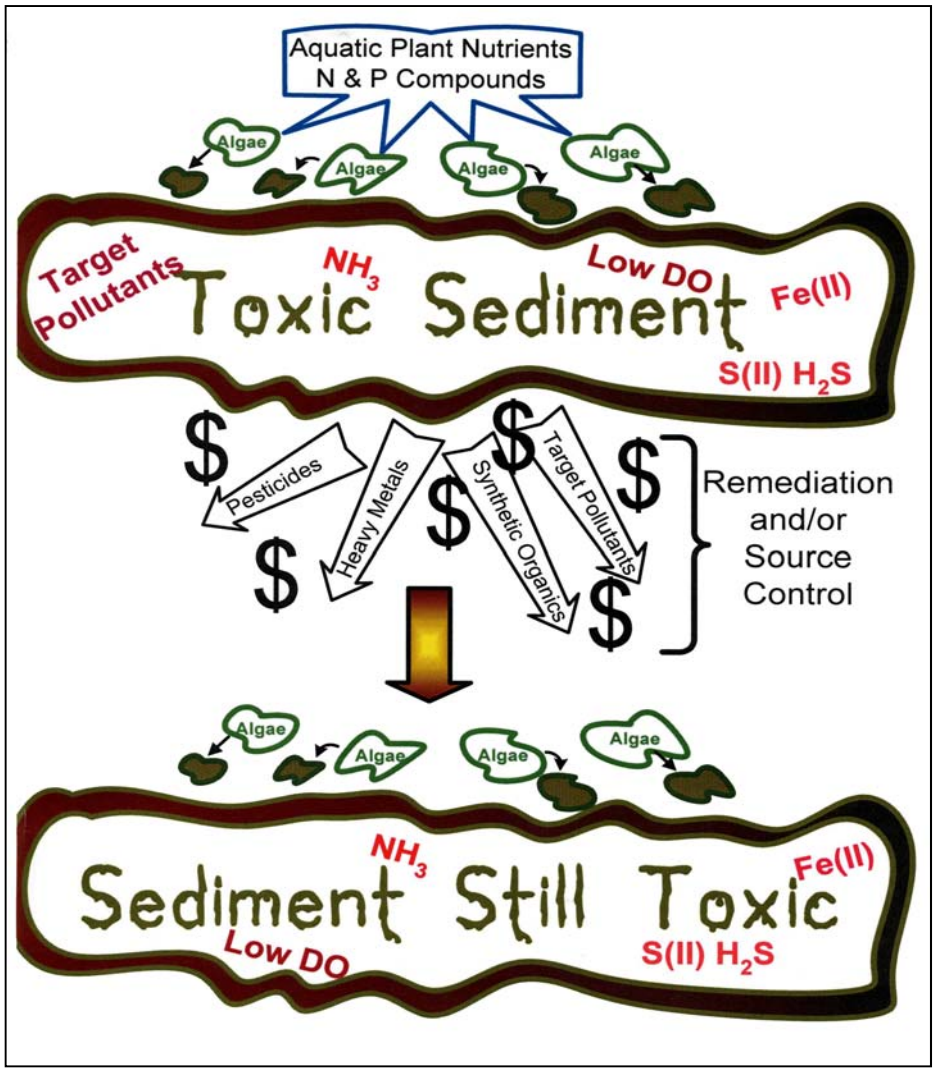

Thus,
Adequate Regulation of Sediment Quality
Must Reliably Consider Toxicity
Enabled by Nutrients
That Develop into Algae
That Create Oxygen Demand
That Gets Exerted in Watercolumn & Sediment to
Be Toxic to Aquatic Life
Create Anoxic Conditions to
Enable Ammonia Toxicity

Figure 3


Aquatic Plant Nutrients
N & P Compounds
Algae
Algae
Algae
Algae
Target Pollutants
NH3
Toxic Sediment
Low DO
Fe(II)
S(II) H2S
$
Pesticides
Heavy Metals
Synthetic Organics
Target Pollutants
Remediation and/or Source Control
Algae
Algae
Algae
Algae
Sediment Still Toxic
NH3
Fe(II)
Low DO
S(II) H2S