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

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This issue of the Newsletter updates previous Newsletter discussions of **pyrethroid-based pesticides** in urban stormwater runoff and presents new information on these pesticides in domestic wastewaters as a cause of **aquatic life toxicity**. In addition, updates are provided on the potential environmental impacts of the pesticide, **Imidacloprid**, and potential environmental issues associated with **nanomaterials**. Information is presented on a new book on **environmental modeling of pollutants.**

Updated Information of Pyrethroid Based Pesticides in Urban Stormwater Runoff

Several previous Stormwater Runoff Water Quality Newsletters NL 8-1/2, 8-6, 9-3, 9-4, 9-6, 9-7, 9-8, 10-3, 10-8, 10-12, 11-3, 11-4, and 11-7/8 have discussed that the pyrethroid-based pesticides are causing aquatic life toxicity in the receiving waters for the runoff. These and other past Newsletters and an index are available at, http://www.gfredlee.com/newsindex.htm. During the mid to late 1990s S. Taylor of RBF Irvine, California and Drs. G. Fred Lee and Anne Jones-Lee conducted studies of pesticide aquatic life toxicity in the Upper Newport Bay watershed in Orange County, California. They found toxicity to aquatic life caused by both organophosphorus-based and pyrethroid-based pesticides. As discussed in their reports, available on the website, www.gfredlee.com in the Surface Water Pesticide subsection at, http://gfredlee.com/pswqual2.htm#pesticide at the time of their studies according to the California Department of Pesticide Regulation about 25,000 lbs (ai)/each year of pyrethroid-based pesticides were used in Orange County, California. However, as reported by Lee and Jones-Lee based on samples collected by Dr. V. Connor of the Central Valley Regional Water Quality Board staff, processed by University of California Davis Aquatic Toxicology Laboratory and with support in part by the DeltaKeeper,

> Lee, G.F. and Jones-Lee, A., "City of Stockton Urban Stormwater Runoff Aquatic Life Toxicity Studies," presented at the NorCAL SETAC annual meeting in Santa Cruz, CA, June (2001). http://www.gfredlee.com/Runoff/stockton-slides_0601.pdf
>
> Lee, G. F. and Jones-Lee, A, "Review of the City of Stockton Urban Stormwater Runoff Aquatic Life Toxicity Studies Conducted by the CVRWQCB, DeltaKeeper and the University of California, Davis, Aquatic Toxicology Laboratory between 1994 and 2000," report to the Central Valley Regional Water Quality Control Board and the DeltaKeeper, submitted by G. Fred Lee & Associates El Macero, CA, November (2001). http://www.gfredlee.com/Runoff/stockton-txt_0401.pdf

aquatic life toxicity in city of Stockton. California urban stormwater runoff could be accounted for in mid to late 1990s based on the concentrations of the organophosphorus pesticides, diazinon and chlorpyrifos. There was no aquatic life toxicity in this runoff that could be attributed to pyrethroid-based pesticides. Based on the Lee and Taylor work in the Upper Newport Bay watershed and the switch to the use of pyrethroid-based pesticides for residential use that occurred as a result of the US EPA restricting the use of organophosphorus based pesticides in urban areas that occurred in the early 2000s, Lee predicted that there would be widespread toxicity in urban streams due to runoff of pyrethroid based pesticides. For a number of years, the focus of studies of pyrethroid-based pesticide aquatic life toxicity was on sediments, to the exclusion of the water column. It was repeatedly pointed out that significant aquatic life toxicity should be expected from pyrethroid-based pesticides in urban stormwater runoff water column that should be investigated.

Recently, Dr. D. Weston of the University of California, Berkley made presentations to the California Central Valley Regional Water Quality Control Board staff and others and in an abbreviated presentation to the UP3 Urban Pesticide Committee on his studies on pyrethroid based aquatic life toxicity in the water column in the Central Valley of California. His PowerPoint slides for this presentation are available on the UP3 website, http://www.up3project.org/up3_upc.shtml. A summary of the Weston et al. studies as prepared by Weston is presented below.

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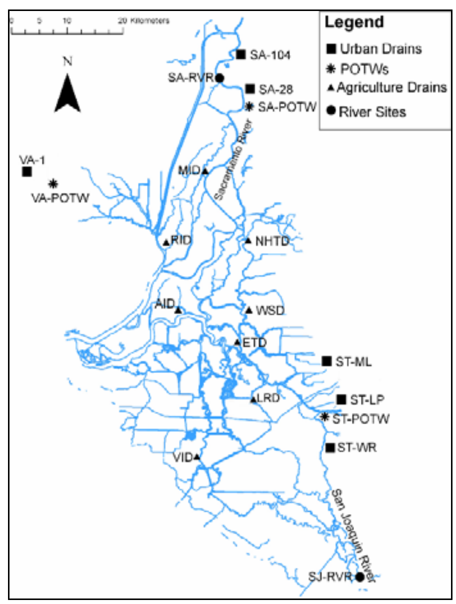
"Pyrethroid Pesticides in the Sacramento-San Joaquin Delta:
Sources and impacts on Delta waters

Donald Weston, University of California, Berkeley
Michael Lydy, Southern Illinois University
Contact: dweston@berkeley.edu

Support for this work was provided by the Central Valley Regional Water Quality Control Board through the Surface Water Ambient Monitoring Program (SWAMP).

OBJECTIVE: To better understand sources of pyrethroid insecticides to the Delta, and to examine their effects on the water bodies in to which they are released.

STUDY APPROACH



- Pyrethroid insecticides are widely used in agricultural and urban settings. California agriculture uses 355,000 lb/yr, and nonagricultural uses comprise another 567,000 lb/yr. Retail sales are not included but would be added to the non-agricultural use.
- To better understand sources of pyrethroids to the Delta, we sampled 8 agricultural pump stations, 6 urban runoff pump stations or storm drains, 3 municipal wastewater treatment plants, and the Sacramento and San Joaquin Rivers as they enter the Delta.
- Potential sources were sampled on 3-5 occasions in the dry season of 2008, and 3 occasions in the wet seasons of 2008 or 2009.
- Transects were sampled along Ulatis Creek, Alamo Creek, American River, San Joaquin River, and Sacramento River as they passed through urban areas, after 2-4 rain events.
- Samples were analyzed for pyrethroids and water toxicity testing was done with a native crustacean, *Hyalella azteca*. For

several of the pyrethroids, a concentration of only 2 parts pyrethroid in a trillion parts water (2 ng/L) is sufficient to cause paralysis in *Hyalella.*

RESULTS: URBAN RUNOFF

- Virtually all urban runoff contained pyrethroids, typically at about 4 times the concentration that would paralyze *Hyalella*.
- Not surprisingly given these pyrethroid concentrations, nearly all urban runoff samples caused toxicity when *Hyalella* was exposed to the water.
- A Toxicity Identification Evaluation (TIE) was done on 7 runoff samples to help determine the cause of toxicity. Results were consistent with pyrethroids as the cause of toxicity in every case.
- Bifenthrin and cyfluthrin are the pyrethroids of greatest toxicological concern in urban runoff. Both are used by professional pest control firms and are also available in retail stores.
- Urban runoff quality was comparable in all communities studied (Sacramento, Stockton, Vacaville), suggesting the conclusions can be extrapolated to urban runoff in general.

RESULTS: MUNICIPAL WASTEWATER

- Pyrethroids were present in about 2/3 of the final effluent samples from wastewater treatment plants.
- They were found most often, and in highest concentration, at the Sacramento treatment plant, followed by Vacaville, and then Stockton.
- The typical wastewater treatment plant effluent contains pyrethroids at about 0.5-1.5 times the concentrations that cause *Hyalella* paralysis.
- Toxicity was seen in every sample from the Sacramento facility and never seen at Stockton. TIE results were not always definitive, but in general, indicate pyrethroids were a significant cause of toxicity.
- The Sacramento plant was the largest single discharger of pyrethroids among all Delta discharges studied, usually releasing at least 10 g/day. A storm water pumping station releases about 3 g/d.

RESULTS: AGRICULTURE

- Agricultural discharges occasionally contained detectable pyrethroids (about 30% of samples).
- Toxicity to *Hyalella* was seen in about 10% of the agricultural samples, and in every case, could be linked to the pyrethroid lambda-cyhalothrin or the organophosphate insecticide, chlorpyrifos.
- Input of pyrethroids from the agricultural pump stations is difficult to quantify, but is probably well under that of an urban pump station in most cases.

RESULTS: RECEIVING WATERS

- Ulatis Creek and Alamo Creek were sampled following two storms. Before entering Vacaville, there were no detectable pyrethroids in either creek and only one sample (of 6) had slight toxicity. As the creeks left the city, they contained 4-10 times the concentration of pyrethroids that cause paralysis in *Hyalella*, and all samples caused high toxicity.
- The American River was sampled from Folsom Lake to the Sacramento River confluence after several storms. Toxicity to *Hyalella* was found repeatedly, extending over 20 miles of the river on one occasion and intermittently over 30 miles on another. The pyrethroid bifenthrin appeared responsible.
- Toxicity in the American River was compounded by the low flows maintained in the river by low releases from Folsom Dam during February and March (800 cfs). Thus, there was less water in the river to dilute the bifenthrin-containing runoff. There was no toxicity following a May rain when flows were over 4000 cfs.

- In the San Joaquin River, one sample on the downstream edge of Stockton was toxic to *Hyalella*, probably due to bifenthrin. We have no data to determine how far down the river the effect extended.
- Pyrethroids (most often bifenthrin) were found in the Sacramento River as it passed through the city of Sacramento. Concentrations peaked near the threshold of causing toxicity. No toxicity was seen, probably because the times of elevated bifenthrin concentrations occurred concurrently with high suspended sediments that reduced its availability to organisms.
- Release of pyrethroid insecticides from urban centers is sufficient to adversely affect water quality over considerable lengths of small to moderate size water bodies (up to the American River in size). In the larger water bodies (Sacramento and San Joaquin Rivers), localized impacts are possible after a typical storm event."

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It is clear that urban stormwater runoff in the Central Valley, and likely elsewhere, is highly toxic to some forms of aquatic life due pyrethroid-based pesticides used on residential and commercial properties. The pyrethroid-based pesticides are causing aquatic life toxicity in the watercolumn during runoff events and, following the events, are causing toxicity to some forms of aquatic life in sediments.

Aquatic life toxicity in Central Valley waterbodies is not new. From at least the 1980s until the early 2000s the toxicity was caused by organophosphorus pesticides, such as diazinon and chlorpyrifos. Studies by Central Valley Regional Water Qualitty Board staff (Drs. C. Foe and V. Connor) found toxicity in the Sacramento and San Joaquin Rivers and the Delta due to organophosphorus pesticides used in urban and agricultural areas. As noted above, when the US EPA banned the use of those pesticides for urban use in the early 2000s in order to protect the health of children, pesticide manufactures switched to pyrethroid-based pesticides. While it is in the interest of environmental quality protection to properly evaluate potential impacts of proposed substitute pesticides before their use, this was not done. In fact, as discussed in reports on the Lee and Jones-Lee website [www.gfredlee.com in the Surface Water Pesticide Toxicity section at http://gfredlee.com/pswqual2.htm#pesticide], the US EPA Office of Pesticide Programs (US EPA OPP) in Washington, D.C. and the California Department of Pesticide Regulation (DPR) allow the registration and use of pesticides on residential properties from which runoff can be expected despite the fact that those pesticides will cause toxicity to some forms of aquatic life in the urban streams and other waterbodies. In order to control such toxicity and to comply with the requirements of the Clean Water Act, there is need to change the approach for regulating pesticide use to prevent the substitution of a banned pesticide/use with one that causes the same or even greater aquatic life problems. This issue was discussed more than 8 years ago in the Lee and Jones-Lee papers and reports with summaries in past issues of this Newsletter.

Lee, G. F., "The Urban Pesticide Problem: How Do We Know the Substitutes Aren't Worse Than the Ones They're Replacing?" Feature Article, *Journal Stormwater* **2(1)**:68-71, Forrester Press, January/February (2001).
http://www.gfredlee.com/Runoff/UrbanPestStormwater1.pdf

Jones-Lee, A., and Lee, G. F., "Proactive Approach for Managing Pesticide-Caused Aquatic Life Toxicity," Report of G. Fred Lee & Associates, El Macero, CA, October (2000).
http://www.gfredlee.com/Runoff/proactivepest_1000.pdf

Because the national and state pesticide regulatory agencies have not taken adequate action to prevent aquatic life toxicity in runoff waters from areas in which the pesticides are used, Jones-Lee and Lee (2002) recommended that when a new or expanded-use pesticide is permitted, local regulatory agencies require the pesticide manufactures to fund studies to assess aquatic life impacts of the pesticide/use in runoff waters from the areas of use.

As discussed below both the US EPA OPP and the CA DPR are now devoting more attention to the aquatic life toxicity problems caused by pesticides registered for use. It is imperative that pesticide registration include a reliable evaluation of fate and transport of pesticides as they may enter the environment associated with their permitted for use/label instructions. Information on the US EPA OPP efforts to begin to address these issues is presented below.

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"*EPA Pesticide Program Updates*
from EPA's Office of Pesticide Programs 06/19/09
http://www.epa.gov/pesticides
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IN THIS UPDATE: New Pyrethrins and Pyrethroid Information Available

Three new items on EPA's Web site will enhance the public's access to information about pesticides in the pyrethrin/ pyrethroid class of insecticides. These items are 1) a new consolidated Web page on these chemicals, 2) a paper and related fact sheet on the Agency's analysis of whether an association exists between pyrethrin/ pyrethroid exposure and asthma and allergies, and 3) a description of new environmental hazard and general labeling for non-agricultural outdoor use pyrethroid products, including tips for consumers to use in reducing the potential for pesticide runoff and drift. The new items are described further below.

EPA's Office of Pesticide Programs (OPP) has launched a new Web site on pyrethrins and pyrethroids. On this site, you can access information about EPA's reevaluation of these pesticides, assessment of pyrethrin and pyrethroid incidents, and other related topics and issues. Pyrethrins and pyrethroids are insecticides included in over 3,500 registered products, many of which are used widely in and around households, including on pets, in mosquito control, and in agriculture. The use of pyrethrins and pyrethroids has increased during the past decade with the declining use of organophosphate pesticides, which are more acutely toxic to birds and mammals than the pyrethroids. This new Web site is available at,
http://www.epa.gov/oppsrrd1/reevaluation/pyrethroids-pyrethrins.html .

Included on this Web site is a new paper on pyrethrin/pyrethroid products and asthma/allergy effects. Differing from previous reviews, this review uses a "weight of the evidence approach" to determine whether there is a clear and consistent association between pyrethrins/pyrethroid exposure and asthma and allergies. From this analysis, the Agency has concluded that there is no clear evidence of an association. For more information on this paper, visit
http://www.epa.gov/oppsrrd1/reevaluation/paw-factsheet.html .

Also included on the new Web site is a page on Environmental Hazard and General Labeling for Pyrethroid Non-Agricultural Outdoor Products. This page describes the revised "Environmental Hazard Statements" and general "Directions for Use" language for pyrethroid pesticide products used in non-agricultural outdoor settings, which affects over 2,000 end-use pyrethroid pesticides. The revised label language will reduce the potential for pesticide runoff and drift of pyrethroid pesticides, ultimately providing better protection to aquatic habitats and the environment. Consumers can begin using these improved practices to protect water resources. Visit http://www.epa.gov/oppsrrd1/reevaluation/environmental-hazard-statment.html to find out more information on this labeling initiative.

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EPA distributes its Pesticide Program Updates to external stakeholders and citizens who have expressed an interest in pesticide activities and decisions. This update service is part of EPA's continuing effort to improve public access to Federal pesticide information.

For general questions on pesticides and pesticide poisoning prevention, contact the National Pesticide Information Center (NPIC), toll free, at: 1-800-858-7378, by E-mail at npic@ace.orst.edu, or by visiting their website at: http://npic.orst.edu/

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CA DPR Re-evaluation Program for Pyrethroid-Based Pesticides

The California Department of Pesticide Regulation is re-evaluating the environmental impact of pyrethroid-based pesticides. Information on that re-evaluation can be found on the DPR website at http://www.cdpr.ca.gov/docs/registration/reevaluation/chemicals/pyrethroids.htm. Updated information on that program is available at the UP3 website at http://www.up3project.org/up3_upc.shtml

Imidacloprid

Stormwater Runoff Water Quality Newsletter Volume 8, no. 1/2 provided information on the new type of pesticides, neonicotinoid pesticides, which are synthetic chemicals having a nicotine-like structure. That Newsletter addressed some of the issues associated with the replacement of the OP pesticides diazinon and chlorpyrifos with pyrethroid and neonicotinoid-type pesticides and noted that several of the neonicotinoid-type pesticides (including Acetacioprid, Imidaclorprid, and Thiamethoxam) are being used in substantial amounts in California agriculture. For example, in 2002, 6,632 pounds (ai) of Acetacioprid, 224,730 pounds (ai) of Imidacloprid, and 11,091 pounds (ai) of Thiamethoxam were used. At the time Lee wrote his Newsletter discussion of neonicotinoid pesticides in February 2005, the preliminary assessment of potential environment impacts of Imidacloprid appeared to show that its residential use as a replacement for chlorpyrifos and diazinon would not likely result in aquatic life toxicity due to its presence in stormwater runoff. However, there was concern about its potential to cause groundwater pollution. The US EPA OPP recently released the following information about Imidaclorprid; additional information on this type of pesticide is available on the Internet by searching, "Imidacloprid."

"*EPA Pesticide Program Updates from EPA's Office of Pesticide Programs 07/13/09*
http://www.epa.gov/pesticides
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EPA Issues Registration Review Final Work Plan for Imidacloprid

EPA has issued a Final Work Plan (FWP) for the registration review of imidacloprid. A neonicotinoid insecticide, imidacloprid is highly toxic to honeybees on an acute exposure basis; however, potential chronic effects on honeybee colonies are uncertain. As part of the registration review process, EPA is requiring field-based data on imidacloprid to better understand its potential impact on pollinators. The Agency also will be working with Federal and State officials, as well as the international community and other stakeholders, to develop data and help us understand the potential impact of the neonicotinoid insecticides on pollinators. For additional information about the Agency's pollinator protections, please see http://www.epa.gov/pesticides/ecosystem/pollinator-protection.html. For information about the registration review of imidacloprid, please see
http://www.epa.gov/oppsrrd1/registration_review/imidacloprid/index.htm.

Imidacloprid is used on food crops, ornamentals, turf, seed treatments, domestic pets, and structural pests. During the public comment period on the Agency's Imidacloprid Summary Document and Preliminary Work Plan (PWP), issued in December 2008, EPA received over 12,000 comments voicing concern over imidacloprid's potential effects on pollinators. The comments highlighted points to be considered during registration review, but did not change the timeline or data requirements set forth in the PWP. The Agency has addressed the comments in three separate Responses to Comments memos. The PWP, response to comments documents, and FWP can be found in the imidacloprid registration review docket, EPA-HQ-OPP-2008-0844, at www.regulations.gov. Please see:

Imidacloprid Summary Document/Preliminary Work Plan: EPA-HQ-OPP-2008-0844-0002
Imidacloprid Final Work Plan: EPA-HQ-OPP-2008-0844-0116"

New Book on Water Quality Modeling
ILM Publications, Glendale, AZ recently published a book entitled, "**Modelling of Pollutants in Complex Environmental Systems**" (2009). That book was edited by Dr. Grady Hanrahan who holds the John Stauffer Endowed Chair of Analytical Chemistry at California Lutheran University in Thousand Oaks, California. As noted in the scan of the book's table of contents that follows, Drs. Anne Jones-Lee and G. Fred Lee were invited to contribute a chapter addressing the modeling of stormwater runoff water quality. Their chapter evolved from a California Water and Environmental Modeling Forum (CWEMF) workshop CWEMF organized several years ago on stormwater runoff modeling during which they found that some of the presenters incorrectly characterized hydrology modeling of stormwater runoff as "stormwater runoff water quality modeling." As discussed in their chapter, in order to properly model ***water quality impacts*** of chemical constituents in stormwater runoff, it is necessary to incorporate aquatic chemistry (thermodynamics and kinetics) and biological effects information. A reference to that chapter is:

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.

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Modelling of Pollutants in Complex Environmental Systems

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Nanomaterials Environmental Impacts

Presented below is recently published information on potential environmental impacts of nanomaterials.

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Transfer of gold nanoparticles from the water column to the estuarine food web

Nature Nanotechnology Published online: 21 June 2009 | doi:10.1038/nnano.2009.157

John L. Ferry[1,2], Preston Craig[1], Cole Hexel[1], Patrick Sisco[1], Rebecca Frey[1], Paul L. Pennington[3], Michael H. Fulton[3], I. Geoff Scott[3], Alan W. Decho[2,4], Shosaku Kashiwada[2,4], Catherine J. Murphy[1,2] & Timothy J. Shaw[1,2]

Abstract

Within the next five years the manufacture of large quantities of nanomaterials may lead to unintended contamination of terrestrial and aquatic ecosystems[1]. The unique physical, chemical and electronic properties of nanomaterials allow new modes of interaction with environmental systems that can have unexpected impacts[2, 3]. Here, we show that gold nanorods can readily pass from the water column to the marine food web in three laboratory-constructed estuarine mesocosms containing sea water, sediment, sea grass, microbes, biofilms, snails, clams, shrimp and fish. A single dose of gold nanorods (65 nm length 15 nm diameter) was added to each mesocosm and their distribution in the aqueous and sediment phases monitored over 12 days. Nanorods partitioned between biofilms, sediments, plants, animals and sea water with a recovery of 84.4%. Clams and biofilms accumulated the most nanoparticles on a per mass basis, suggesting that gold nanorods can readily pass from the water column to the marine food web.

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California Department of Toxic Substance Control (DTSC): Nanotechnology Listserv

"*The Environmental Defense Fund (EDF) blog post "Hiding a toxic nanomaterial's identity: TSCA's disappearing act" looks at the issue of confidential business information under the Toxic Substances Control Act (TSCA). BASF submitted a notice in July 2008 "...reporting toxic effects at very low doses of a carbon nanotube (CNT) observed in a 90-day rat inhalation study. In that notice, BASF had declared the specific identity of its CNT to be confidential business information, hence denying that information to the public.*

Recently, BASF researchers published a paper in the journal of Toxicological Sciences on the results of a 90-day rat inhalation study for a multi-walled carbon nanotube material (Nanocyl

NC 7000). The question asked on the EDF blog is "So why, then, did BASF claim the identity of its nanomaterial to be confidential when submitting the same study to EPA?"
The complete EDF blog post is available at: http://blogs.edf.org/nanotechnology/2009/07/14/hiding-a-toxic-nanomaterials-identity-tscas-disappearing-act/ The abstract published in the journal of Toxicological Sciences can be viewed at:http://toxsci.oxfordjournals.org/cgi/content/abstract/kfp146v1

More information on BASF Safety Research on Nanomaterials can be found at: http://www.basf.com/group/corporate/en/content/sustainability/dialogue/in-dialogue-with-politics/nanotechnology/knowledge/safety-research

To subscribe to the DTSC: Nanotechnology listserv, please go to http://www.calepa.ca.gov/Listservs/dtsc/. For information on DTSC regulations, as well as other relevant developments go tohttp://www.dtsc.ca.gov/LawsRegsPolicies/index.cfm"