SCIENCE OF THE TOTAL ENVIRONMENT 389 (2008) 87–100

available at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/scitotenv

Comparison of storm intensity and application timing on modeled transport and fate of six contaminants

*Erica D. Chiovarou**, *Thomas C. Siewicki*

Center for Coastal Environmental Health and Biomolecular Research, National Ocean Service, NOAA, 219 Fort Johnson Rd., Charleston, SC 29412-9110, USA

ARTICLE INFO

Article history:
Received 6 March 2007
Received in revised form
15 August 2007
Accepted 17 August 2007
Available online 27 September 2007

Keywords:
Storms
Modeling
Transport
Fate
St. Johns River
Johnson Creek

ABSTRACT

Hundreds, if not thousands, of fish kills and kills of other aquatic organisms occur following storms in the US each year, but they are difficult to quantify, investigate, or manage due to the transient nature of major storms and the other priorities following them. Methods are needed to better understand the causes of these kills. The Pesticide Root Zone Model and the Exposure Analysis Modeling System were used to compare risk to resident biota in estuarine headwaters in two locations under various conditions. Contaminants were selected using a landuse-based preliminary risk assessment approach. Atrazine, fipronil, and imidacloprid were compared for potential impacts on important prey species, including copepods and grass shrimp, in Lake Bethel in Volusia County, Florida. Carbaryl, diquat dibromide, and fluoranthene were compared for potential impacts on salmon and other aquatic species in Johnson Creek, near Portland, Oregon. Predictions of contaminant concentrations in groundwater runoff, surface water, benthic sediments, and pelagic biota tissue were obtained based upon watershed characteristics, storm types, and contaminant chemistry and application. For all six contaminants, the simulated concentrations were highest following the 100-yr storms and lowest following the 2-yr storms. Aqueous concentrations ranged between 84 and 2100% higher in 100-yr compared to two-yr storms. Most atrazine and carbaryl concentrations were highest if applied one day before the storm while fipronil, imidacloprid, and diquat dibromide were highest if applied 16 days prior to the storm. Carbaryl and fluoranthene concentrations were highest in the forested segment of the watershed while diquat dibromide concentrations were highest in the agricultural segment. In Florida simulations, groundwater and surface water concentrations generally were highest for atrazine, followed by imidacloprid, and then fipronil. Atrazine poses the highest risk to algae and copepods due to its mobility and high allowable application rates. Fipronil and imidacloprid, though highly toxic, were not predicted to occur at high enough concentrations to pose a risk. In Oregon simulations, groundwater and surface water concentrations generally were highest for carbaryl, followed by fluoranthene, and then diquat dibromide. For salmonids, fluoranthene poses a higher risk than carbaryl, whereas it is unlikely that diquat dibromide will affect salmonids in this system. For crustaceans, carbaryl poses the greatest risk, followed by fluoranthene. Diquat dibromide was determined to pose little risk. These tests demonstrate the use of preliminary risk assessment, along with transport and fate modeling, to characterize risks to aquatic organisms without the need for in situ chemical measurements.

Published by Elsevier B.V.

* *Corresponding author*. Tel.: +1 843 762 8527; fax: +1 843 762 8700.
E-mail address: Erica.Chiovarou@noaa.gov (E.D. Chiovarou).

0048-9697/$ – see front matter. Published by Elsevier B.V.
doi:10.1016/j.scitotenv.2007.08.029

1. Introduction

Natural resource agencies are concerned that heavy coastal storms routinely result in unreported, widespread loss of fish and shellfish. Fish kills after heavy rainfall are common occurrences in coastal states. In 2004, Florida, Maryland, and South Carolina reported 490, 122, and 80 fish kills, respectively (FWC, 2006; MDE, 2006; Personal Communication, Kevin Godwin, Environmental Health Manager, SCDHEC, Columbia, SC). Most fish kills likely go unreported as there are no structured programs to look for fish kills following major climatic events and because resource agencies are typically responding to higher priority emergencies.

It is often difficult to identify the cause of a specific fish kill partly because of the large number of potential causes, including dissolved oxygen depletion, disease, and contaminant runoff. The latter is the focus of this study. In 2006, there were 30 million unique substances in the Chemical Abstracts Registry System (ACS, 2006). About 4000 new items are added to the registry each day. Many chemicals are not regulated by EPA. Over 40% of high-production chemicals have had no toxicity or environmental fate tests, and only 7% have had all basic toxicity and fate tests (EPA, 2004b). It is impossible to measure all toxic chemicals in all estuaries. There is a compelling need to develop methods that help identify the causes of fish kills associated with coastal storms and that are applicable to a variety of coastal settings. Such a methodology must consider the influence of the magnitude and timing of the rain event relative to contamination of the nearby upland.

The purpose of this study was to demonstrate a method of using transport and fate models to address the risks from contaminated stormwater runoff. Six contaminants were selected using a preliminary risk assessment. Atrazine is the second most widely used pesticide in the United States and is applied to agricultural and residential areas (Kiely et al., 2004). It has been detected in ground and surface waters, including coastal surface water (Fulton et al., 2004). Imidacloprid and fipronil are insecticides of increasing use as they are identified by the US Environmental Protection Agency as alternatives to organophosphate compounds (EPA, 2002b). Both of these insecticides are highly toxic to marine organisms (Key et al., 2007). Carbaryl is an insecticide often used to control mosquitoes and, in the state of Washington, can be applied directly in estuaries to control burrowing shrimp. Over a million pounds of carbaryl are used annually in the US (EPA, 2004a). Diquat dibromide is an herbicide used at 500,000 lb annually in the US in both aquatic and terrestrial settings (EPA, 2002a). Fluoranthene is a nearly ubiquitous, toxic polycyclic aromatic hydrocarbon often present as a result of combustion of fossil fuels. The source of most coastal urban surface water fluoranthene is roadway runoff, and this runoff has been implicated as contributing to deaths of spawning salmon (Personal Communication, Nathaniel Scholz, NOAA Fisheries, Northwest Fisheries Science Center, Ecotoxicology and Environmental Fish Health Program, Seattle, WA). This study used transport and fate modeling to estimate risks to resident biota from these six contaminants following different storm intensities.

2. Methods

2.1. *Approach*

For this study, a landuse-based preliminary risk assessment of potential contaminants was conducted at two pilot study areas: the upper St. Johns River in Florida and the lower Columbia River in Washington and Oregon. Data on potential application rates or expected runoff concentrations, along with physical–chemical properties and known toxicity, were collected for contaminants permitted in each of the study areas. Three contaminants at each site were chosen for transport and fate modeling based upon amount used within the watershed, known toxicity to susceptible organisms, as well as contaminant persistence and mobility. An important consideration was the overall lack of critical information for pesticides with increasing use within the watersheds. A common toxic polycyclic aromatic hydrocarbon (PAH) was selected in the Oregon study because of the association of roadway runoff, containing fossil fuel combustion products, with deaths of spawning salmon.

We compared potential risks to sensitive aquatic resources under different storm types, different time periods between the application of pesticides and the storm events, and different predominant land cover types by using the US Environmental Protection Agency Pesticide Root Zone Model (PRZM) (Carsel et al., 1995) and Exposure Analysis Modeling System (EXAMS) (Burns, 2001). The combination of PRZM and EXAMS was used to estimate the potential for shallow surface- and groundwater introduction of three pesticides into a headwater of Florida's St. Johns River and the introduction of two pesticides and one PAH into Oregon's Johnson Creek. The watersheds for each study area were delineated using the ArcGIS Hydro Data Model (Arc Hydro) (Maidment, 2002). In addition, an assessment of the potential for these contaminants to cause negative impacts on resident biota was conducted. The results reported herein are predicted concentrations from these deterministic, predictive models that are based upon core mechanistic process equations. Risks to dominant prey species, including copepods and grass shrimp, at the Florida study area and to salmonids at a restored urban historical spawning stream in Oregon are evaluated. Comparisons of modeling results to available toxicity data are also discussed.

2.2. *Study sites*

The Florida headwater, Lake Bethel (Fig. 1a), is a shallow (1 m average depth, 86 ha area) brackish-water lake on the upper St. Johns River in Volusia County. The 2259 ha watershed is characterized by changing land uses, including a large amount of residential housing. EXAMS traditionally calculates transport though segments of a stream network, so in order to model this lake watershed, Lake Bethel was segmented in the model based upon proximity to the shoreline (Fig. 2a). The Oregon headwater, known as Johnson Creek above Regner Station (Fig. 1b), is an urbanized freshwater stream near the city of Portland that historically provided habitat to spawning salmon. The creek was divided into three segments according