Modeling the atmospheric deposition and stormwater washoff of nitrogen compounds

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Abstract

We investigated the suitability of integrating deterministic models to estimate the relative contributions of atmospheric dry and wet deposition onto an urban surface and the subsequent amounts removed by stormwater runoff. The CIT airshed model and the United States Environmental Protection Agency Storm Water Management Model (SWMM) were linked in order to simulate the fate and transport of nitrogen species through the atmosphere and storm drainage system in Los Angeles, California, USA. Coupling CIT and SWMM involved defining and resolving five critical issues: (1) reconciling the different modeling domain sizes, (2) accounting for dry deposition due to plant uptake, (3) estimating the fraction of deposited contaminant available for washoff, (4) defining wet deposition inputs to SWMM, and (5) parameterizing the SWMM washoff algorithm. The CIT–SWMM interface was demonstrated by simulating dry deposition, wet deposition, and stormwater runoff events to represent the time period from November 18, 1987 to December 4, 1987 for a heavily urbanized Los Angeles watershed discharging to Santa Monica Bay. From November 18th to December 3rd the simulated average dry deposition flux of nitrogen was 0.195 kg N/ha-day to the watershed and 0.016 kg N/ha-day to Santa Monica Bay. The simulated rainfall concentrations during the December 4th rainfall event ranged from 3.76 to 8.23 mg/l for nitrate and from 0.067 to 0.220 mg/l for ammonium. The simulated stormwater runoff event mean concentrations from the watershed were 4.86 mg/l and 0.12 mg/l for nitrate and ammonium, respectively. Considering the meteorology during the simulation period, the CIT and SWMM predictions compare well with observations in the Los Angeles area and in other urban areas in the United States. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Atmospheric deposition; Stormwater modeling; Air quality; Water quality

Software availability
(1) Program title: Storm Water Management Model (SWMM)
Contact address: US Environmental Protection Agency (EPA), Center for Exposure Assessment Modeling (CEAM). www.epa.gov/ceampubl/softwdos.htm
Programming language: Fortran 77
Hardware requirements: IBM PC
Cost: Free, limited technical support
(2) Program title: CIT Airshed Model
Contact address: Professor Armistead (Ted) Russell,
School of Civil and Environmental Engineering, Georgia Institute of Technology. www.environmental.gatech.edu/~trussell/page.html
Programming language: Fortran 77
Hardware requirements: Unix Workstation or PC with Fortran compiler
Cost: Nominal, no support

1. Introduction

The earth’s population is increasing at a rate of approximately 1.45% annually and is tending to concentrate more and more in coastal and riparian areas (LANL,
In 1960, approximately 80 million people lived in coastal areas of the United States. As of 1990, 112 million people lived in US coastal areas, and projections indicate 127 million people will live on the US coast by 2010. Southern California Counties are projected to be among the leaders in absolute population change (Culliton et al., 1990). Increased human population and population density in coastal areas have placed increased pressure on coastal ecosystems. One impact that has been well studied in the past decade in the United States and elsewhere is direct and indirect inputs to water bodies from atmospheric deposition (US EPA, 2000; Hicks, 1997). In particular, research has focused on quantifying the atmospheric inputs of nitrogen compounds to coastal water bodies (e.g., Weaver et al., 1999; Scudlark et al., 1998; Fisher and Oppenheimer, 1991; Hinga et al., 1991).

The input of biologically available nitrogen compounds to surface waters can produce several deleterious water-quality impacts (Jickells, 1998; Novotny and Olem, 1994). Excessive nitrogen inputs in the form of ammonium (NH$_4^+$), nitrite (NO$_2^-$), nitrate (NO$_3^-$), and organic nitrogen compounds to sunlit and quiescent water bodies that are nitrogen limited could accelerate the growth of phytoplankton and macrophytes. Increased frequency of phytoplankton blooms could lead to the development of hypoxic conditions (reduced oxygen levels) or anoxic conditions (complete lack of oxygen) in water bodies. Moreover, altered nutrient dynamics could result in loss of species diversity, fundamental changes to ecosystem structure, and toxic algal blooms (US EPA, 2000; Hicks, 1997). These conditions can adversely affect aquatic life and the associated beneficial uses of water bodies.

Nitrogen compounds can enter a water body via tributaries, overland flow, subsurface flow, atmospheric dry and wet deposition, storm drainage systems, and discharges from industrial and municipal wastewater treatment facilities. The effective management of water bodies receiving this variety of inputs requires accurate knowledge of pollutant sources and transport pathways. The problem is inherently multimedia requiring an integration of atmospheric, watershed, and water body processes. Information produced by integrated airshed–watershed–water body monitoring and modeling studies is imperative to understand and analyze such complex problems and to develop and evaluate linked airshed–watershed management plans.

Because of its size and economic and political importance, Chesapeake Bay is probably the most studied large water body from an integrated airshed–watershed–water body perspective. Research has focused on the quantification of direct atmospheric deposition loadings and indirect loadings from deposition onto the watershed (Garrison et al., 1999; Dennis, 1997; Fisher and Oppenheimer, 1991; Fisher et al., 1988), identification of nitrogen sources (Russell et al., 1998), and linked airshed–watershed modeling (Wang et al., 1997; Linker and Thomann, 1996). Results from these studies and others have indicated that atmospheric deposition accounts for approximately 27% of the nitrogen load to the bay. The atmospheric deposition component includes the loading from direct wet and dry deposition onto the bay and the indirect loading from dry and wet deposition onto the bay watershed.

Atmospheric deposition has also been found to account for a significant fraction of the total nitrogen loading to other coastal water bodies. In Florida, studies have determined that approximately 26% of the nitrogen load to Sarasota Bay and 28% of the nitrogen load to Tampa Bay comes from atmospheric deposition and indirect loading from deposition onto the watershed (Valigura et al., 1996). In the northeast United States, atmospheric deposition accounts for approximately 20% of the total nitrogen load to Long Island Sound (Hu et al., 1998; Valigura et al., 1996).

Besides monitoring studies, several integrated airshed–watershed–water body modeling studies have been performed in the past decade. The Chesapeake Bay Program has been especially active in performing integrated modeling efforts to identify the sources of nutrient inputs to the bay and to determine the relative importance of atmospheric deposition. For example, Wang et al. (1997) determined the wet deposition of nitrate and the dry deposition of nitrate, organic nitrogen, organic phosphorus, and dissolved organic phosphorus to the Chesapeake Bay watershed. These deposition values were used as inputs to the Phase IV Chesapeake Bay Watershed Model. In another modeling analysis, E.H. Pechan and Associates, Inc. (1996) evaluated the effects of various NOx emission reductions on the nutrient inputs to the Chesapeake Bay. They utilized a projected 2005 emissions inventory developed as input to the US Environmental Protection Agency’s (EPA) Regional Oxidant Model (ROM). Nitrate deposition by bay subwatershed was estimated by converting NOx emissions to deposition using source-receptor coefficients determined by repeated runs of the Regional Acid Deposition Model (RADM). The Chesapeake Bay Watershed Model then estimated nitrate loading to the bay from the nitrate deposition amounts.

Studies of pollution inputs to the Great Lakes have also used integrated airshed–watershed–water body modeling. The mass balance studies of the EPA Great Lakes Program (e.g. Lake Michigan Mass Balance Study; EPA Great Lakes Program, 2000) link transport and transformation models to study the changes in concentrations in the air, water, soil, and biota that would result from changes in loading. The goal of the effort is to provide a scientific basis for the determination of load reductions to meet their desired quality objectives.

One of the goals for linking atmospheric deposition
models and watershed models is to determine the relative contribution of the total loading to water bodies resulting from atmospheric deposition. Pollutants can essentially follow two transport pathways from the atmosphere to the water body; one is through direct deposition or diffusion and the other is through deposition/diffusion to the watershed and subsequent washoff during rainfall events. By determining the direct and indirect contribution from atmospheric deposition, appropriate integrated air–water quality management plans can be formulated and implemented. The research efforts described above have produced significant advances in integrated airshed–watershed–water body modeling, but there is still a need for further research to reduce uncertainty and improve the accuracy of integrated modeling efforts (Hicks, 1998).

This paper describes a research effort to link an air chemistry model and an urban runoff model to simulate the fate and transport of nitrogen compounds through the atmosphere and storm drainage system of the Los Angeles Basin. The goal of the project was to develop an operational linkage between the CIT airshed model (Russell et al., 1988; McRae et al., 1982) and the US EPA Storm Water Management Model (SWMM) (Huber and Dickinson, 1988). Nitrogen compounds were selected for this demonstration because they are important in both the air and water environments (Ellis, 1986), they have been shown to be detrimental to coastal water quality (Jickells, 1998), and data were available to test the model linkage for the Los Angeles Basin.

In the linkage described here, the CIT model, using an air emissions inventory and meteorological data, simulates the fate and transport of nitrogen compounds and other photochemical pollutants in the atmosphere. SWMM simulates the stormwater runoff flow rates and relevant nitrogen compound concentrations from drainage subcatchments and the flow and transport of the nitrogen compounds to the outlet of the storm drainage system. In this paper we describe CIT and SWMM, we discuss the steps we took and assumptions we made to provide a preliminary linkage, and we apply the CIT–SWMM linkage to a demonstration problem. For the demonstration we determine the relative contributions of pollutant loading to Santa Monica Bay from: (1) direct dry deposition, (2) direct wet deposition, (3) dry deposition onto a watershed washed into the bay by surface runoff, and (4) wet deposition onto a watershed that becomes part of the surface runoff.

2. Model descriptions

CIT is an Eulerian-based model and solves the transport and chemical reactions of pollutants in the atmosphere using a numerical solution scheme for a set of 35 reacting chemical species (Russell et al., 1988; McRae et al., 1982). It contains 106 chemical kinetic equations and implements the Lurmann, Carter, and Coyner lumped molecule chemical mechanism. CIT requires (1) land use and an emissions inventory defined over the modeling grid and (2) wind, temperature, and atmospheric boundary layer depth information from measurements or produced by meteorological models to compute spatially-averaged hourly values of atmospheric concentrations of many gaseous air pollutants and aerosols. The area to be modeled is divided into horizontal grids typically 5-km by 5-km with up to 10 terrain-following vertical grid levels. CIT contains a resistance-based dry deposition module and predicts deposition fluxes that can be integrated over time to yield estimates of total deposition of specified compounds for each grid cell.

SWMM is a comprehensive deterministic stormwater runoff simulation program capable of simulating the transport of precipitation and pollutants washed off the ground surface, through pipe/channel networks and storage/treatment facilities, and finally to receiving waters (Nix, 1994). Given soil imperviousness and a temporal and spatial distribution of rainfall, SWMM calculates the infiltration and surface storage of water and routes the rest as sheet flow. Pollutant concentrations are calculated in the sheet flow using empirical buildup/washoff algorithms or a defined rating curve function. The sheet flow is routed to storm drain inlets and then to the discharge point using either the kinematic wave approximation or the full Saint-Venant Equations (Huber and Dickinson, 1988; Roesner et al., 1988). Primary model inputs are (1) the temporal and spatial distribution of rainfall, (2) drainage catchment characteristics including area, percent imperviousness, slope, depression storage, and drainage path roughness, and (3) storm drain information including drain geometry, slope, and roughness. The SWMM outputs of interest include time series of flow rates and contaminant concentrations and other characteristics of the stormwater runoff at selected points in the storm drainage system.

3. CIT–SWMM linkage issues

The transport of atmospherically deposited chemical compounds through the terrestrial biosphere is presently an area of great uncertainty (Hicks, 1998; Valigura et al., 1996). Potentially, an accurate representation of the airshed and watershed in CIT and SWMM and a physically precise linkage between the two models will reduce the degree of uncertainty. A significant amount of research is still required to accurately describe the retention/transfer of a contaminant from the airshed through the watershed to the receiving water body. This initial linkage of detailed deterministic airshed and watershed models is an effort to clarify many of the issues involved in linked airshed–watershed modeling.
The CIT–SWMM linkage is predicated on the assumption that dry and wet deposition to a water body or onto a watershed are the removal mechanisms for atmospheric pollutants. Dry deposition involves the turbulent and gravitational transfer of pollutants from the air to the underlying surface during dry weather. Wet deposition refers to the droplet processes that scavenge material from the atmosphere during precipitation events and deposits them on the surface. Removal processes on the surface (e.g. street sweeping, resuspension and relocation, plant uptake), nuisance flows) can reduce the amount of deposited material available for washoff during the next rainfall-runoff event.

In the CIT–SWMM linkage, CIT calculates the dry deposition flux of nitrogen compounds originating from airborne emissions at hourly intervals. The fluxes are summed over the simulated dry weather period to obtain the total load deposited to the land and water surfaces. CIT also calculates concentrations of contaminants in the atmosphere at each time step. At the start of a rainfall event, the concentrations computed at that time step are vertically averaged and used in our calculation of wet deposition. SWMM then simulates the washoff and transport of the dry-deposited material and the transport of the material in the precipitation through the stormwater drainage system to the watershed outlet.

Although the link between CIT and SWMM is seemingly straightforward, the former produces mass fluxes of contaminants to the surface per 25-km² grid cell, while the later utilizes mass loads on a per subcatchment basis. The grid cells and subcatchments do not, in general, correspond one-to-one since they are based on different information. Therefore, the integration of CIT and SWMM requires several assumptions concerning the transformation of CIT output into SWMM input. In addition, the CIT calculation of dry deposition was devised to estimate the removal from the atmosphere, not the amount depositing on the watershed available for washoff. In general, the latter will be smaller due to such sink mechanisms as resuspension and plant uptake. Another issue is that SWMM estimates the buildup and washoff of contaminants on urban surfaces, but does not differentiate the source of the buildup, i.e. atmospheric deposition versus residential fertilizer application. Additional issues include the determination of the wet deposition load based on atmospheric concentrations prior to the storm event and the parameterization of the SWMM washoff algorithm. Hence, our interfacing of CIT and SWMM involved defining and resolving five critical issues that are discussed in the following five subsections: (1) reconciling the different modeling domain sizes, (2) accounting for dry deposition due to plant uptake, (3) estimating the fraction of deposited contaminant available for washoff, (4) defining wet deposition inputs to SWMM, and (5) parameterizing the SWMM washoff algorithm.

3.1. Modeling domain

The two models linked in this research operate on different size domains. As an atmospheric chemistry-transport code, CIT is dependent on local and regional meteorology. Therefore, its modeling domain is on the order of thousands of square kilometers, while the domain of SWMM can vary, but typically is less than hundreds of square kilometers. The modeling domain of CIT is divided horizontally into 5-km by 5-km grid cells. The SWMM modeling domain is divided into subcatchments based on drainage patterns that generally have irregular shapes. In most cases, one CIT grid cell contains tens to hundreds of SWMM subcatchments. Except for large-scale modeling efforts, a single CIT grid cell would contain the entire SWMM modeling domain. The CIT–SWMM linkage therefore is currently most appropriate for large-scale modeling projects, such as the one demonstrated in this paper. CIT calculates dry deposition flux per grid cell based on many factors including land cover and meteorological conditions. Because the calculated dry deposition value is not appropriate for direct use in SWMM, it was adjusted according to the methodology described in the next subsection.

3.2. Dry deposition resulting from plant uptake

CIT simulates the major forms of atmospheric nitrogen deposition including nitric acid (HNO₃), ammonium nitrate (NH₄NO₃), ammonia (NH₃), nitrogen oxides (NOx), peroxyacetyl nitrate (PAN), and alkyl nitrate aerosols (see Table 1). A major issue is the fate and transport of these compounds in the water and soil following dry and wet deposition. The fate of the deposited material is a function of the phase of the chemical, the deposition surface, and processes at the soil surface and in the water. In this study, we are concerned with the available fraction of the deposited nitrogen compounds, i.e. the amount of dry and wet deposition available for entrainment into surface water runoff during a rain

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solubility (Henry’s law coefficient, M atm⁻¹, at 298K)</th>
<th>Contribution after dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>2.1×10⁹</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td>PAN</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>NH₄</td>
<td>6×10⁻⁶</td>
<td>NH₄⁺</td>
</tr>
<tr>
<td>NO₂</td>
<td>1.9×10⁻⁹</td>
<td></td>
</tr>
<tr>
<td>NO₃</td>
<td>1.0×10⁻²</td>
<td></td>
</tr>
<tr>
<td>NH₄NO₃ aerosol</td>
<td>High</td>
<td>NH₄⁺, NO₃⁻</td>
</tr>
<tr>
<td>Alkyl nitrate aerosols</td>
<td>Low</td>
<td></td>
</tr>
</tbody>
</table>

*Solubility greatly enhanced by acid–base equilibria in acidic droplets.
event. We estimated the available fraction based on the best available information on the processes affecting the fate and transport of each compound.

In general, the dry deposition process is due to settling of particulates onto the surface, plant uptake, diffusion, and chemical reactions at the surface. We have assumed that the fraction of dry deposition due to plant uptake is not available for washoff. CIT computes dry deposition flux from all three processes summed together. Therefore, we had to remove the plant uptake fraction when transferring the dry deposition values from CIT to SWMM.

NH₃ is a gaseous compound whose dry deposition is primarily a result of plant uptake and surface adsorption. To estimate the fraction of the calculated dry deposition due to plant uptake we determined the fraction of each CIT grid cell covered by vegetation. We also estimated the deposition velocities to vegetated surfaces and impervious urban areas for unstable meteorological conditions. We then calculated a fraction of the deposited material taken up by plants using the following formula:

\[
 WF = \frac{V_{d_{veg}} \cdot P_{veg}}{V_{d_{veg}} \cdot P_{veg} + V_{d_{urb}} (1 - P_{veg})}
\]

where WF is the fraction of the deposited material assumed to be removed by plant uptake, \( V_{d_{veg}} \) is the estimated deposition velocity to vegetated surfaces [length per time], \( P_{veg} \) is the percent of vegetated surface area in the CIT grid cell, and \( V_{d_{urb}} \) is the estimated deposition velocity to urban surfaces [length per time]. The weighting factor estimates the amount of deposition to vegetated surfaces, which approximates the fraction of NH₃ deposition due to plant uptake. We assumed the fraction of dry deposited NH₃ to pervious surfaces not taken up by plants to be assimilated into the soil matrix and the small fraction of dry deposited NH₃ to impervious urban surfaces to remain on the surface until the next rainfall-runoff event.

Gaseous PAN and NOx were assumed to be unavailable for washoff because their dry deposition is due primarily to plant uptake (i.e. WF=1). PAN and NOx are also relatively insoluble in water, so that the small fraction of the deposited material not taken up by plants is considered unavailable for entrainment in stormwater runoff. Furthermore, the dry deposition flux of PAN and NOx is low relative to HNO₃ and NH₄NO₃, so that their contribution to the total nitrogen load is minimal.

Considering HNO₃ and NH₄NO₃, studies have shown that the surface resistance to these compounds is relatively small and does not depend on the land cover to a great extent (i.e. \( V_{d_{veg}} \approx V_{d_{urb}} \)) (Hanson and Lindberg, 1991; Dollard et al., 1987). Thus, we assumed that the spatial distribution of dry deposition of HNO₃ and NH₄NO₃ onto vegetated surfaces is strictly proportional to the fraction of each grid cell covered by vegetated surfaces.

CIT calculates mass flux per unit area in each grid cell for each simulated compound. To link the CIT output with the SWMM model the deposition flux is integrated over a specified dry-weather period prior to a precipitation event and the fraction of dry deposition due to plant uptake is subtracted from the total. The amounts of deposited compounds not due to plant uptake, i.e. the amounts available for washoff, are then translated into the dissolved-phase compounds of interest, nitrate (NO₃⁻) and ammonium (NH₄⁺), using stoichiometric relationships. The computed amounts of NO₃⁻ and NH₄⁺ are then input to the SWMM model as the pollutant loads from dry deposition available for washoff at the beginning of the storm event.

3.3. Availability of deposited nitrogen compounds for washoff

A material that can be removed from a surface by stormwater runoff is said to be available for washoff. Many factors can inhibit the washoff of a contaminant including armoring, surface texture, and spatial distribution of contaminant. These individual factors are not accounted for in SWMM. We do not address them in this research, but their effect, if present, would be to reduce the amount of nitrogen compounds washed off. Besides inhibiting factors, several other processes in addition to plant uptake can remove the deposited nitrogen compounds during the dry period before the next rainfall event. The processes (e.g. street sweeping, resuspension and relocation, removal in nuisance flows) depend greatly on what land cover the material deposits onto and are specific to the area of study. Since we do not have monitoring data to represent these processes, we take a conservative approach and estimate the removal of the total deposited nitrogen compounds by these processes to be zero. In addition, because we are focusing on nitrogen compounds of atmospheric origin, we do not consider ground-level sources of nitrogen (e.g. residential fertilizer use, animal wastes, plant decay) in the simulations.

3.4. Wet deposition

Wet scavenging is best described in two parts, that occurring within the cloud (rainout) and that occurring below the cloud (washout) (Engelmann, 1971). The processes of below-cloud scavenging are better understood and more experimental data are available than for in-cloud scavenging processes. Studies of the concentrations of ionic compounds throughout precipitation events also suggest the first part of a storm scavenges contaminants from the atmosphere in an initial washout process. Subsequent rainfall passes through a cleaner
atmosphere and concentrations are generally found to decrease (Hendry and Brezonik, 1980). The simulation of the rainout and washout processes and the time-variable atmospheric concentrations is extremely complex. Developing and implementing an algorithm representing the individual scavenging processes is beyond the scope of the present research project. A simpler method is to group the individual processes together into a bulk-scavenging ratio to estimate wet-deposition fluxes.

The concept of scavenging ratios is based on the simplified assumption that the concentration of the component in precipitation is related to the concentration of the respective compound in the air (Kasper-Giebl et al., 1999; Engelmann, 1971). Algorithms have been developed to use the scavenging ratio concept to estimate the amount of contaminant removed during rainstorms given atmospheric concentrations at the beginning of the rainfall event and other characteristics of the rainfall (e.g. raindrop size, intensity) and contaminant (e.g. size, solubility, Henry’s law constant). In our research we used a formulation developed by Slade (1968) to represent the washout of aerosols and gaseous pollutants (Novotny and Olem, 1994):

\[
D_{\text{wet}} = C_{\text{air}}(1 - \exp(-\lambda t))H \tag{2}
\]

where \(D_{\text{wet}}\) is the wet deposition per unit area [quantity per unit area], \(C_{\text{air}}\) is the atmospheric concentration before the rain event [quantity per unit volume], \(\lambda\) is the washout coefficient, \(t\) is the duration of rainfall [time], and \(H\) is the depth of atmosphere through which the pollutant plume is mixed [length]. The value for \(C_{\text{air}}\) is calculated by CIT for each grid cell by finding the average atmospheric concentration over \(H\). The washout coefficient is a function of rainfall intensity and was determined at each time step using relationships from Slade (1968). More complex rainout and washout algorithms exist, but their implementation in the CIT–SWMM linkage was beyond the scope of this phase of the research project. It should be noted that results obtained with Eq. (2) were nearly identical to a 100% washout assumption due to the nature of the rain event.

Nitrogen in precipitation is most often present as ammonium (\(\text{NH}_4^+\)), nitrate (\(\text{NO}_3^-\)), and dissolved organic nitrogen (DON) (Russell et al., 1998; Halverson et al., 1984; Hendry and Brezonik, 1980; Huff, 1976). For our study we are interested in the quantity of \(\text{NH}_4^+\) and \(\text{NO}_3^-\) entering water bodies directly and indirectly from atmospheric deposition. \(\text{NH}_4^+\) in precipitation is a result of the dissolution of atmospheric \(\text{NH}_3\) gas and the scavenging of \(\text{NH}_4^+\) aerosol, and \(\text{NO}_3^-\) in precipitation results mostly from the dissolution of \(\text{HNO}_3\). In the CIT–SWMM linkage, we assume the PAN, alkyl nitrate, and NOx contributions to \(\text{NH}_4^+\) and \(\text{NO}_3^-\) concentrations in rainfall are negligible because of their relative insolubility. The other major nitrogen deposition compounds simulated by CIT, namely \(\text{HNO}_3\), \(\text{NH}_2\text{NO}_3\), and \(\text{NH}_3\), all dissolve readily in water at pH values commonly observed in precipitation and stormwater runoff. Therefore, we will assume that each contributes to the \(\text{NH}_4^+\) and \(\text{NO}_3^-\) rainfall concentrations.

Contaminant concentrations in rainfall can be represented in SWMM, but the code does not allow for time-variant rainfall concentration. As an approximation, we have computed the average concentration in the rainfall over the entire storm event by dividing the calculated wet deposition masses of \(\text{NO}_3^-\) and \(\text{NH}_4^+\) by the total precipitation volume during the storm event. A time-variable rainfall concentration would be more appropriate, but implementing this formulation in the SWMM code was not possible in the time frame of the project. Although a constant rainfall concentration might not result in accurate representations of within storm runoff concentrations, the overall storm event load should be accurately estimated.

3.5. Parameterizing the SWMM washoff algorithm

Stormwater washoff of deposited material is not well understood. Deposited nitrogen compounds are mostly smaller-sized particulates or gaseous material that reacted with the surface. Pitt (1987) found most of the small-sized pollutant fraction to be available for washoff from impervious surfaces. Based on this observation, we assumed the gaseous and relatively small-sized nitrogen aerosols present on the impervious surfaces from dry deposition were all available for washoff and as stated above we ignored washoff inhibitors (e.g. armoring). The SWMM washoff algorithm applies the following relationship to each subcatchment (Huber and Dickinson, 1988):

\[
P_{\text{off}}(t) = -\frac{dP}{dt} = R_c \cdot r(t) - P_p(t) \tag{3}
\]

where \(P_{\text{off}}(t)\) is the rate at which pollutant is washed off the subwatershed [quantity per time], \(R_c\) is a washoff coefficient, \(r(t)\) is the runoff rate over the subcatchment [length per time], \(n\) is the washoff power, and \(P_p(t)\) is the amount of pollutant \(p\) on the subcatchment [quantity]. The initial \(P_p\) is the CIT-computed deposition load on each subcatchment corrected for plant uptake and summed over the dry weather period. SWMM calculates \(r\) at each time step, while \(R_c\) and \(n\) are input parameters that should be defined through calibration to site-specific monitoring data. Since we did not have the proper calibration data to define \(R_c\) and \(n\), we used values recommended by the SWMM user’s manual. A future field experiment in Los Angeles will attempt to define these parameters more accurately.
4. Case study

We selected the Ballona Creek watershed in Los Angeles, California, USA, to demonstrate the CIT–SWMM interface. Ballona Creek drains approximately 300 km² (116 mi²) of the 3500 km² (1350 mi²) heavily urbanized Los Angeles Metropolitan Area. Ballona Creek has been found to be the most significant source of nonpoint source pollution to the Santa Monica Bight (Suffet et al., 1997; Wong et al., 1997). The creek begins as a covered storm drain in downtown Los Angeles and it eventually becomes an open concrete-lined trapezoidal channel with a bottom width of 25 to 60 m (80 to 200 ft). As it travels westward through Los Angeles towards the coast, additional storm drains contribute flow and pollutants.

The Ballona Creek watershed is composed of three primary drainage catchments: the Ballona Creek, the Sepulveda Channel, and the Centinela Creek catchments (see Fig. 1). We display a part of Santa Monica Bay in Fig. 1 to indicate the proximity of the Ballona Creek watershed to the bay. The Ballona catchment creates the headwater of Ballona Creek. Sepulveda Channel and then Centinela Creek discharge into Ballona Creek within a mile of the edge of the Ballona catchment. From the confluence of Centinela Creek and Ballona Creek to the outlet to Santa Monica Bay is approximately 5 km. The runoff contribution to Ballona Creek along these 5 km is small from Marina Del Rey to the North and from what remains of the Ballona Wetlands to the South.

The Ballona Creek watershed is hilly upstream, but flat near the outlet. In the hilly areas, the ground slope is as high as 30 to 50%. In the flat areas, the ground slope is generally between 1 and 3%. The watershed is more than 85% urban land use with approximately 38% of the impervious surfaces directly connected to the storm drainage system. The imperviousness value was estimated by attributing percent impervious characteristics for the Los Angeles area to specific land uses (Wong et al., 1997; Hydroscience, Inc., 1979). Using a more detailed land classification than shown in Fig. 1, Table 2 shows the total area and percent imperviousness of each land use within the Ballona Creek watershed.

The CIT modeling domain was divided horizontally into 960 5-km by 5-km grid cells centered over the Santa Monica Bay watershed and vertically into five variable height layers ending at 1100 m. The Santa Monica Bay

<table>
<thead>
<tr>
<th>Land use</th>
<th>Area (hectares)</th>
<th>Percent of total</th>
<th>Percent impervious*</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-density residential</td>
<td>5066</td>
<td>16.8</td>
<td>68</td>
</tr>
<tr>
<td>Medium-density</td>
<td>12019</td>
<td>39.9</td>
<td>42</td>
</tr>
<tr>
<td>Low-density residential</td>
<td>1167</td>
<td>3.9</td>
<td>20</td>
</tr>
<tr>
<td>Industrial</td>
<td>1233</td>
<td>4.1</td>
<td>91</td>
</tr>
<tr>
<td>Institutional</td>
<td>1433</td>
<td>4.8</td>
<td>30</td>
</tr>
<tr>
<td>Open space</td>
<td>3743</td>
<td>12.4</td>
<td>0</td>
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<tr>
<td>Transportation</td>
<td>659</td>
<td>2.6</td>
<td>92</td>
</tr>
<tr>
<td>Commercial</td>
<td>3580</td>
<td>11.9</td>
<td>92</td>
</tr>
<tr>
<td>Parks/public</td>
<td>998</td>
<td>3.3</td>
<td>0</td>
</tr>
<tr>
<td>Other/unknown urban</td>
<td>78</td>
<td>0.3</td>
<td>80</td>
</tr>
</tbody>
</table>

*Estimates based on Hydroscience, Inc. (1979) and Wong et al. (1997).
portion of the CIT modeling domain included 121 grid cells extending from the Ballona Creek watershed 50 km west over the Pacific Ocean and 20 km east inland. Fig. 2 shows the 45 CIT grid cells overlying the Ballona Creek watershed and adjacent areas. To drive the wet deposition and stormwater runoff models, we obtained 15-minute interval rainfall records from three rain gauges: the Los Angeles Civic Center (LACC), the Los Angeles International Airport (LAX), and Sepulveda Dam. These gauges were selected because they fell within or very near the catchments. We assumed that the LACC, LAX, and the Sepulveda Dam gauges represented the rainfall on the Ballona, Centinela, and Sepulveda catchments, respectively. The recorded rainfall is assumed to be spatially constant over each catchment. This assumption is satisfactory for this demonstration of the CIT–SWMM linkage, but using rainfall data with better spatial resolution would improve the accuracy of the results.

The SWMM input data required for the Ballona Creek watershed stormwater quality model included subcatchment and storm drainage system information. The subcatchment information consisted mostly of land use and surface characteristics. The storm drainage system data consisted mostly of physical information available in as-built drawings. We obtained 1993 land use information for parts of southern California from the Southern California Association of Governments (SCAG) and the storm drainage system information from microfiche copies of construction drawings at the Los Angeles County Department of Public Works (LADPW). We digitized 2899 storm drains with a total length of 365 km (225 mi) into a GIS environment. The total drainage area of 300 km² (116 mi²) was divided into 1897 subcatchments based on topography and drainage patterns.

The time period from November 18, 1987 to December 4, 1987 was selected as the case study time period. A rainstorm occurred in Los Angeles on November 17, 1987 and although the recorded rainfall amount was less than 2.5 mm (0.1 in) we assumed all the atmospherically deposited material present on the catchment was removed during the storm. The meteorology from November 18th to December 2nd was consistent with normal Los Angeles Basin patterns with primarily westerly wind flows from the coastal areas to the eastern valleys. August 27, 1987 had meteorological conditions consistent with November 18th to December 2nd and we had information available to parameterize CIT. Therefore, we simulated August 27, 1987 to provide results representative of the normal Los Angeles onshore meteorology and the time period from November 18th to December 2nd.

The meteorology on December 3rd was significantly different than that observed from November 18th to December 2nd. The meteorological conditions on December 3rd had increasing offshore wind flow, but insufficient to push the atmospheric contaminants out to sea. Consequently, high aerosol and nitrate levels were observed during the SCAQS (Southern California Air Quality Study), stagnating over the western part of the basin including the Ballona Creek watershed. We simulated the December 3rd deposition event to incorporate the unusual meteorological conditions into the case study.

We assumed the August 27, 1987 simulation results to represent an average deposition day in Los Angeles for the 15-day time period from November 18 to December 2, 1987. Thus, we multiplied the deposition amounts from August 27th by 15 to estimate the total dry deposition for the 15-day time period. This summation was then added to the calculated December 3rd deposition to estimate the total deposition leading up to the December 4th rainfall event. The December 4th rainfall event produced an average of 26 mm (1.03 in) of rainfall in the Ballona Creek watershed. The rainfall records from the three rain gauges mentioned above were used to drive the SWMM model to simulate the December 4th storm event and determine the amount of dry deposited material washed off.

The CIT model and setup for both the August 27th and the December 3rd simulations were identical to those in an earlier analysis of the SCAQS (Harley et al., 1993). Meteorological data collected during the August 27, 1987 and December 3, 1987 SCAQS monitoring episodes were used to determine mixing heights and 3-D

![Fig. 2. The 45 CIT grid cells overlying the Ballona Creek watershed and adjacent areas. The entire CIT modeling domain has 960 grid cells centered on the Ballona Creek watershed.](image-url)
fields of meteorological variables. The 1987 emissions inventory was used. A test case was run for the late August 1987 episode to ensure that the model was operating properly.

5. Results

CIT calculated dry deposition over its entire grid cell structure. We extracted the hourly dry deposition amounts for the 22 grid cells that cover the Ballona Creek watershed for the August 27, 1987 and the December 3, 1987 simulations. The dry deposited amounts of nitrogen compounds were converted into NO$_3^-$ and NH$_4^+$ based on how the various nitrogen compounds would react with rainfall and stormwater (see Table 1). For the August 27th simulation, the average NO$_3^-$ and NH$_4^+$ loads available for washoff from the Ballona Creek watershed were 0.04 g/m$^2$ (0.36 lb/acre) and 0.0009 g/m$^2$ (0.008 lb/acre), respectively. For the December 3rd dry deposition simulation, the average NO$_3^-$ and NH$_4^+$ loads were 0.12 g/m$^2$ (1.1 lb/acre) and 0.002 g/m$^2$ (0.018 lb/acre), respectively. These dry deposition results and the others shown below incorporate the weighting factor to remove the fraction of dry deposition due to plant uptake.

Figs. 3 and 4 show the spatial distribution of the NO$_3^-$ and NH$_4^+$ dry deposition loads per unit area (amount available for washoff), respectively, for December 3, 1987. The spatial distribution of the August 27th dry deposition is not shown because it is similar to the December 3rd pattern, but the deposition magnitudes are reduced. From Figs. 3 and 4 we see the deposited loads are greater over the watershed than over Santa Monica Bay. The nitrogen dry deposition flux to the watershed for August 27th was 0.10 kg N/ha-day (0.09 lb N/acre-day) and for December 3rd was 0.27 kg N/ha-day (0.24 lb N/acre-day). For the entire simulation period, the total atmospheric loading to the watershed from November 18 to December 3, 1997, was 0.73 g/m$^2$ (6.4 lb/acre) of NO$_3^-$ and 0.015 g/m$^2$ (0.13 lb/acre) of NH$_4^+$.

Unfortunately, dry deposition measurements of nitrogen compounds are very rare for urban Los Angeles. Consequently, for comparison we must use data from rural areas near Los Angeles to compare to our simulated results. Takemoto et al. (1995) reported an average daily dry deposition flux of 0.063 kg N/ha-day (0.056 lb N/acre-day) in the general Los Angeles area. Their flux is based on results from the California Acid Deposition Monitoring Program (CADMP) and includes HNO$_3$, NO$_x$, NH$_3$, and NO$_3^-$. Our August 27th flux is higher than the flux estimated by Takemoto et al. (1995) even with the plant uptake fraction removed, but this is expected because our value includes additional nitrogen compounds not accounted for in the CADMP. The December 3, 1987 flux is approximately four times greater than the average daily value, but this is expected because of the nature of the meteorology and associated level of photochemical pollution. Russell et al. (1993) used CIT to determine the dry deposition flux of nitrogen compounds to the Los Angeles Basin for August 30–31, 1982. They reported the nitrogen deposition flux at the San Dimas Experimental Forest near Los Angeles to be 0.18 kg N/ha-day (0.16 lb N/acre-day) on August 31, 1982. Their flux is slightly smaller than our calculated dry deposition flux of 0.27 kg N/ha-day (0.24 lb N/acre-day) for December 3, 1987, but this is expected because our location was heavily urbanized and much closer to emission sources than their location. For additional comparison, Shahin et al. (1999) estimated the average dry deposition flux of nitrogen compounds to an urban area in Chicago, Illinois, USA, between May and October 1997 to be 0.034 kg N/ha-day (0.03 lb N/acre-day), a value nearly one-third of our simulated value for August 27, 1987. This difference is consistent with the observations of Takemoto et al. (1995), who found the dry deposition flux of nitrogen to urban sites in California to be up to 17 times greater than the flux to eastern US sites.

The simulated wet deposition loads of NO$_3^-$ and
NH$_4^+$ onto the Ballona Creek watershed during the December 4th rainfall event were 38,500 kg (84,800 lb) and 950 kg (2050 lb), respectively. The average NO$_3^-$ concentration in the precipitation was 8.23 mg/l for the Centinela catchment, 3.75 mg/l for the Sepulveda catchment, and 4.88 mg/l for the Ballona catchment. For NH$_4^+$, the simulated concentrations were 0.22 mg/l for the Centinela catchment, 0.067 mg/l for the Sepulveda catchment, and 0.125 mg/l for the Ballona catchment. The simulated NO$_3^-$ concentrations are higher than the average observed concentration of 1.42 mg/l from 1985 to 1990 in Pasadena, California, which is about 15 miles Northeast (inland) from the Ballona Creek watershed (Blanchard and Tonnessen, 1993). But the simulated NO$_3^-$ concentrations are within or slightly below the range of observations (6.2 to 31.3 mg/l) for urban industrial regions in the United States and Europe compiled by de Luca et al. (1991). The relatively high simulated NO$_3^-$ concentrations compared to the Los Angeles area average are expected because of the high level of nitrogen compounds prior to the start of the December 4, 1987 storm event. The simulated NH$_4^+$ concentrations agree better with observations near Los Angeles and throughout the United States than the NO$_3^-$ concentrations. The simulated NH$_4^+$ concentrations are slightly less than the 0.37 mg/l observed in Pasadena, California, from 1985 to 1990 (Blanchard and Tonnessen, 1993), and 0.35 mg/l observed in the Long Island Sound from April 1991 to December 1993 (Hu et al., 1998), but similar to the 0.16 mg/l observed in Gainesville, Florida (Hendry and Brezonik, 1980).

The NO$_3^-$ and NH$_4^+$ loads to the watershed over the 16-day dry weather period and the 6-hour storm event and the amounts washed off during the storm are given in Table 3. According to the stormwater runoff simulation approximately 60% of the rainfall is calculated to become runoff, which is in agreement with results reported by Stenstrom (1999) for the Ballona Creek watershed. The runoff from pervious surfaces was almost negligible for the storm event simulated. The stormwater runoff simulation assumed that the nitrogen compounds in the runoff do not react with the watershed during overland flow or transport through the storm drainage system. Thus, because 60% of the rainfall becomes runoff we know that 60% of the total NO$_3^-$ and NH$_4^+$ load deposited during the rainfall event is discharged. Approximately 88% and 90% of the total NO$_3^-$ load and total NH$_4^+$ load, respectively, in the stormwater runoff is from the precipitation. The high fraction of NO$_3^-$ and NH$_4^+$ load from precipitation in stormwater runoff agrees with observations by Halverson et al. (1984) for urban paved surfaces in Pennsylvania and Miller and Mattraw (1982) for urban areas in Florida.

The results indicate that only 1.4% of the dry deposited NO$_3^-$ and 1.3% of the dry deposited NH$_4^+$ was washed off during the storm event. This is a relatively small fraction. If all the dry deposited material available for washoff had been washed off, the concentrations of NO$_3^-$ and NH$_4^+$ in the runoff would have been well above reasonable values. Therefore, it is clear that either (1) the dry deposition was overestimated or (2) the mechanisms present in the watershed to remove or fix NO$_3^-$ and NH$_4^+$ (e.g. street sweeping, resuspension and relocation, nuisance flows) are significant and should have been accounted for in the simulation. We have relatively good confidence in the predicted dry deposition loads because the amounts were compared to other studies. Therefore, it appears that the watershed

<table>
<thead>
<tr>
<th>Amount on watershed available for washoff (kg)</th>
<th>Amount washed off (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3$ wet deposition: 38,500</td>
<td>21,700</td>
</tr>
<tr>
<td>NO$_3$ dry deposition: 220,100</td>
<td>3000</td>
</tr>
<tr>
<td>NH$_4$ wet deposition: 950</td>
<td>530</td>
</tr>
<tr>
<td>NH$_4$ dry deposition: 4600</td>
<td>60</td>
</tr>
</tbody>
</table>
processes reducing the amount available for washoff are indeed significant and should be accounted for in linked airshed—watershed modeling.

The event mean concentrations (EMCs) of the stormwater runoff event on December 4, 1987 were calculated by dividing the total mass of contaminant discharged during the storm event by the total volume of water discharged. To evaluate the predictions we can compare the predicted NO$_3^-$ and NH$_4^+$ EMCs from the Ballona Creek catchment of the Ballona Creek watershed with observations from the LADPW stormwater monitoring program. The predicted NO$_3^-$ and NH$_4^+$ EMCs were 4.9 and 0.13 mg/l, respectively, and the average NO$_3^-$ and NH$_4^+$ EMCs for 14 storm events monitored from 1996 to 1998 during the LADPW stormwater monitoring program were 3.68 and 0.627 mg/l, respectively (LADPW 1998, 1997). The predicted EMC for NO$_3^-$ is 33% higher than the average observed EMC, but this was expected because of the high photochemical pollution level leading up to the December 4th storm event. The predicted EMC for NH$_4^+$ is nearly 80% less than the observed EMC, which indicates that an important source of NH$_4^+$ is probably present in the watershed and was not accounted for in the simulation.

Fig. 5 shows the relative percent contributions of NO$_3^-$ and NH$_4^+$ to Santa Monica Bay from four sources during the case study time period of November 18 to December 4, 1987: (1) direct dry deposition, (2) direct wet deposition, (3) dry deposition onto the Ballona Creek watershed washed into the bay by surface runoff, and (4) wet deposition onto the Ballona Creek watershed that becomes part of the surface runoff. The results displayed in Fig. 5 indicate that wet deposition directly to the bay is a significant proportion of NO$_3^-$ loading for this 17-day period, whereas direct dry deposition to the bay is the major source of NH$_4^+$. The results represent a 17-day period in late November and early December during the 1987 wet season and extrapolation to annual loads for comparison to other studies is not possible. The CIT–SWMM interface should be used to simulate several years of dry deposition, wet deposition, and stormwater runoff before estimating average annual values.

Table 4 shows the NO$_3^-$ and NH$_4^+$ wet and dry deposition fluxes to the watershed and to Santa Monica Bay for the entire 17-day simulation time period. The wet deposition flux was found by dividing the total mass deposited during the rainfall event by the average storm duration of 6 hours and the areas of the watershed or bay. The surface area of the bay is roughly 2.25 times larger than the surface area of the Ballona Creek watershed. The NO$_3^-$ wet deposition fluxes to the bay and to the watershed are nearly equal, suggesting that the concentrations of NO$_3^-$-containing compounds over the bay are approximately equal to the concentrations over the watershed. This is expected because nitric acid and other compounds containing NO$_3^-$ are terminal compounds—that is, they have little, if any, further atmospheric reactions and they have a relatively long atmospheric lifetime. Thus concentration gradients are smoothed out. Ammonia, on the other hand, is very reactive and has a much shorter atmospheric lifetime. Thus it will show high concentration near its sources—this results in the higher dry deposition flux to the bay. We can explain this by noting that dry deposition is dependent on the surface resistance and the meteorological characteristics at the location. For some of the nitrate-forming compounds and ammonia gas, the surface resistance of water is several times greater than for land. This results in the higher dry deposition flux to land surfaces for these compounds.

6. Summary

This paper described our initial work to integrate CIT and SWMM to model the urban atmosphere, watershed,

<table>
<thead>
<tr>
<th>Load</th>
<th>NO$_3^-$ (kg/ha-day)</th>
<th>NH$_4^+$ (kg/ha-day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet deposition to bay</td>
<td>5.25</td>
<td>0.038</td>
</tr>
<tr>
<td>Dry deposition to bay</td>
<td>0.057</td>
<td>0.0034</td>
</tr>
<tr>
<td>Wet deposition to watershed</td>
<td>5.15</td>
<td>0.12</td>
</tr>
<tr>
<td>Dry deposition to watershed</td>
<td>0.46</td>
<td>0.0096</td>
</tr>
</tbody>
</table>
and storm drainage system. The first stage of this linkage involved five issues: (1) reconciling the different modeling domain sizes, (2) accounting for dry deposition due to plant uptake, (3) estimating the fraction of deposited contaminant available for washoff, (4) defining wet deposition inputs to SWMM, and (5) parameterizing the SWMM washoff algorithm. We devised a procedure to estimate the fraction of dry deposition due to plant uptake and subtracted that amount from the total mass deposited. We followed a conservative approach and assumed that the amount of dry-deposited nitrogen compounds available for stormwater runoff was not affected by the many potential removal mechanisms.

We demonstrated the CIT–SWMM interface by simulating a dry-weather period from November 18 to December 3, 1987 and a rainfall event of December 4, 1987. The demonstration showed that the deposition of nitrogen compounds on December 3, 1987 was high, consistent with the high air pollution levels and associated meteorology observed on this date. SWMM calculated concentrations of nitrogen compounds in the stormwater runoff event on December 4th that were similar to actual concentrations observed by the Los Angeles County Department of Public Works. The results from this demonstration of the CIT–SWMM interface should not be extrapolated to annual average values. To generate annual average values the CIT–SWMM interface should be used to simulate several years of dry deposition, wet deposition, and stormwater runoff. The CIT–SWMM interface should be thoroughly tested and the linkage components improved before initiating an effort to simulate several years.

Although the present analysis had no cross-disciplinary calibration data and made significant assumptions concerning removal processes and wet deposition, the demonstration showed that the CIT–SWMM interface to be a useful tool for investigating the relative contribution of atmospheric compounds to stormwater runoff and other air–water quality problems. The CIT–SWMM linkage is one component of a more comprehensive integrated urban environmental modeling framework. The overall modeling framework being developed will include regional and mesoscale meteorology, groundwater fate and transport, and receiving-water quality models in addition to the atmospheric chemistry and stormwater runoff models described in this paper. Establishing the link between CIT and SWMM was one of the first objectives in the development of an integrated urban environmental modeling framework.

Acknowledgements

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