AGRICULTURAL WATER MANAGEMENT 86 (2006) 220–228

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/agwat

Chemistry of subsurface drain discharge from an agricultural polder soil

Dean Hesterberg[a,*], *Bram de Vos*[b], *P.A.C. Raats*[c]

[a] *Department of Soil Science, Box 7619, North Carolina State University, Raleigh, NC 27695-7619, USA*
[b] *Alterra, Wageningen University and Research Centre, P.O. Box 47, 6700 AA Wageningen, The Netherlands*
[c] *Wageningen University and Research Centre, c/o Paaskamp 16, 9301KL Roden, The Netherlands*

ARTICLE INFO

Article history:
Accepted 19 July 2006
Published on line 7 September 2006

Keywords:
Reactive transport
Redox
Cation exchange
Calcareous soils
Calcite

ABSTRACT

Protecting groundwater and surface water quality in drained agricultural lands is aided by an understanding of soil physical and chemical processes affecting leaching of plant nutrients and other chemical constituents, and discharge from subsurface drains. Our objectives were to determine which chemical processes most affected discharge of redox-active components and macroelements (mainly base cations) from a subsurface drain, and to assess soil characterization needs for more accurate reactive-transport modeling. We measured the chemical composition of discharge water samples collected for 150 days from a 0.075-ha agricultural field plot on a calcareous polder soil. In light of previously reported two-dimensional, hydrological modeling of subsurface NO_3 and Cl discharge, variations in the dissolved concentrations of Mn, Fe, Ca, Mg, Na, K, HCO_3, and S could be qualitatively understood in terms of hydrology along with oxidation–reduction (redox), precipitation/dissolution, and cation exchange processes. Elevated concentrations of Mn and Fe in the presence of NO_3 during periods of peak flow were consistent with mixing of porewaters from reduced and oxidized soil zones. Discharge samples were supersaturated with respect to pure calcite, and responded only weakly to changes in pH over the measured range of pH 7.2–8.2. Dissolved concentrations of Na, Mg, K, and S depended on their relative affinities for the soil exchanger phase and initial NH_4Cl-extractable concentrations throughout the soil profile. Quantitative prediction of reactive components in drain discharge would require coupling of two-dimensional hydrological modeling with modeling of depth-dependent precipitation/dissolution and cation exchange processes, and redox kinetics.

1. Introduction

Movement of chemicals from soils to groundwater and surface waters determines how agricultural practices influence water quality. Quantitative prediction of chemical movement in soils aids in development of sound management practices for minimizing offsite movement of agricultural chemicals. Chemical transport in soils is affected by water movement with dissolved chemical components, and chemical reactions that distribute components between immobile solids and mobile water phases. Transport of non-reactive (conservative) components is mainly tied to water movement. The majority of studies on soil chemical reaction mechanisms such as the thermodynamics and kinetics of cation exchange, adsorption,

---

[*] *Corresponding author.* Tel.: +1 919 513 3035.
E-mail address: dean_hesterberg@ncsu.edu (D. Hesterberg).

0378-3774/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.agwat.2006.07.003

and precipitation–dissolution are conducted under laboratory conditions that offer more control of variables than is possible in field-scale studies.

Field-scale chemical transport is particularly affected by spatially heterogeneous hydrological, chemical, and biological processes that occur simultaneously, and the net discharge of a chemical component from a given volume of soil depends on the integrated effects of these processes. Quantitatively predicting these effects can best be done using computational models that account for spatial and temporal changes. For example, Grindrod and Takase (1996) illustrated the feasibility of numerically solving fully coupled reactive chemical transport in a model that included multiple spatial dimensions, spatial heterogeneity, and kinetic reactions. Schweich et al. (1993a,b) used chemical equilibrium modeling to predict solute concentration waves in exchanging porous media in the presence or absence of precipitation and dissolution reactions. Gaston et al. (1993) coupled exchange equilibria and solute transport models to describe cation breakthrough curves for soil columns. Coupled equilibrium-transport models lend themselves to scenario calculations to predict mobility of trace elements and other reactive chemical component in soil or ground water aquifers (Hesterberg et al., 1994; Walter et al., 1994).

Jacques et al. (2005) used a comprehensive, reactive-transport model (HP1) to simulate uranium transport through a soil profile. This model coupled a hydrological module for water flow with a geochemical speciation module to account for relevant chemical reactions affecting dissolved U over a sequence of time steps. The hydrological model was that used by De Vos et al. (2000, 2002) for modeling Cl and NO_3 transport in the soil studied here. The geochemical part of the model includes aqueous speciation, gas-aqueous partitioning, precipitation and dissolution equilibrium, oxidation-reduction, surface complexation (adsorption), ion exchange, and kinetic reactions. Quantifying all of these geochemical processes for a set of elements in a given soil would require a large number of reaction parameters, including surface complexation model constants, cation-exchange coefficients, and rate coefficients. Moreover, these parameters will vary spatially, particularly as a function of depth in soils that have distinct horizons with different mineralogical and chemical properties. Conceivably, such models could be simplified if certain chemical processes are dominant. Then the geochemical speciation component of such reactive transport models would require fewer parameters measured for a particular soil.

De Vos et al. (2000, 2002) showed that dissolved NO_3 and Cl concentrations in drain discharge showed opposite trends with discharge rate (Figs. 1 and 2). For these weakly sorbed, anionic soil components, discharge concentrations were strongly coupled to patterns of flow through the soil profile and the vertical distribution of these chemical components in the soil profile. Nitrate mostly decreased with soil depth, while Cl increased with depth and was particularly enriched under the subsurface drain located at approximately 1-m depth (Fig. 3). Two-dimensional water-flow patterns and convective transport modeling showed that drainage water was always a mixture of waters originating from different soil zones, but the relative contributions from zones above and below the drain depended on hydrological conditions (De Vos et al., 2000). During periods of high water table and high discharge rates, a greater proportion of drain water originating from shallower soil zones caused an enrichment in NO_3 from these zones and a depletion of Cl originating from below the drain (De Vos et al., 2000, 2002) (Fig. 2).

For reactive components, one would expect that drain discharge would be further modified by the affinity of chemical components for the soil solids, which might vary with soil properties down a soil profile. For example, Bjerg et al. (1993) and Bjerg and Christensen (1993) found that cation exchange processes in ground water aquifers decreased transport velocities of cations and anions in proportion to their affinities for the exchanger phase (i.e., divalent

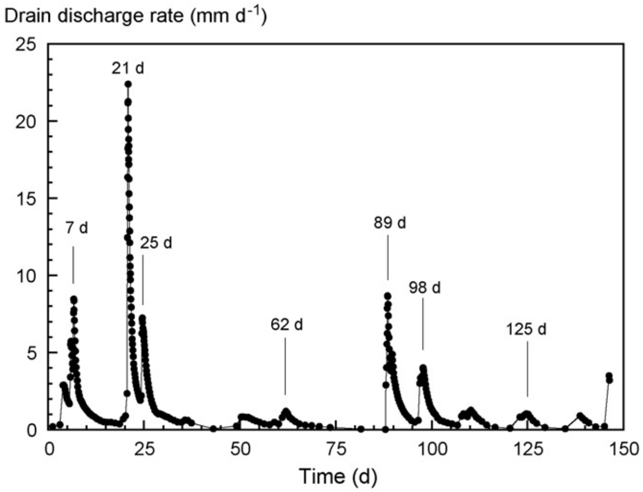

Fig. 1 – Drain discharge rate during 150 d of monitoring of hydrological conditions and drainage-water chemistry at the field site, including data from De Vos et al. (2000). Peak discharge events are denoted as reference times in subsequent figures showing discharge chemistry.

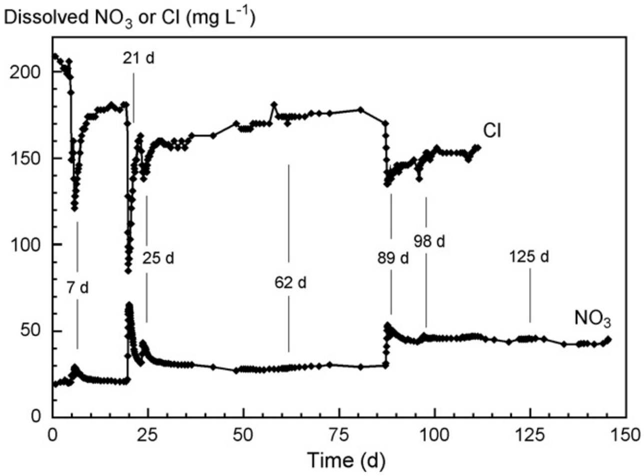

Fig. 2 – Dissolved concentrations of nitrate and chloride in discharge from the subsurface drain over time and in relation to peak discharge rates (denoted—also see Fig. 1) (data from De Vos et al., 2000, 2002).