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Integrated Modeling of Cadmium and Zinc Contamination in Groundwater and Surface Water of the Kempen Region, The Netherlands

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Abstract: Regional modeling of subsurface cadmium and zinc transport in a diffusely polluted area in the south of the Netherlands is the subject of this study. The atmospheric deposition of cadmium and zinc was caused by three zinc-ore smelters (point sources of emission). Agriculture and other sources of heavy metals are small compared to the atmospheric deposition in the vicinity of the smelters. A coupled unsaturated and saturated zone flow and transport model was used to assess and predict reactive transport of cadmium and zinc in three different catchments in the area. For cadmium an extensive set of modeling results is presented, for zinc only preliminary results. The modeling started with a spatial reconstruction of the historic atmospheric deposition followed by an unsaturated zone transport model to calculate cadmium leaching to groundwater. After this, a 3-dimensional reactive transport model was used for the saturated zone. The calculated cadmium concentrations were compared with two datasets of shallow groundwater analyses for validation of the model. The range of modeled and measured concentrations is the same. The modeling results indicate that the amount of cadmium in the groundwater has been doubled in the past twelve years. In the saturated zone, cadmium becomes strongly retarded, despite the low reactivity of the sandy sediments. The maximum depth of modeled and measured concentrations is about 20 meter beneath surface level. In 2002 about 10% of the total estimated leached cadmium has been discharged in seepage areas. The integrated modeling system developed here can be used to run future scenarios to predict resulting concentrations in groundwater and surface water.

Keywords: groundwater; modeling; cadmium; zinc; Netherlands

1. INTRODUCTION

In the border region of Belgium and the Netherlands, three zinc-ore smelters are located within 10 km from each other and a fourth was shut down in 1973. Exhaust fumes from these smelters have emitted oxides of heavy metals during about one century, which have reached the soil either by dry deposition or with rainfall. As a result of this, the soils in the Kempen are heavily contaminated with cadmium and zinc on a large regional scale (Fig. 1) (Sonke, 2002, Harmsen, 1977; Boekholt, 1992). Since the seventies, the cadmium and zinc emissions have been greatly reduced, so the pollution of the soil of this region is of a historical nature.

Leaching of heavy metals from the topsoil is a major risk for groundwater contamination. The soils of the Kempen region are developed in poor aeolic drift sands and are vulnerable for leaching due to the acidifying conditions (Wilkens & Loch, 1997). The saturated zone consists of unconsolidated sandy Pleistocene deposits.

Regional modeling of subsurface cadmium and zinc transport in the diffusely polluted area is the subject of this study. A coupled unsaturated and saturated zone groundwater flow and transport was used for three different catchments the area (Fig. 1) to assess and predict:

- leaching of metals from unsaturated zone to groundwater;
- the development of the metal concentrations in shallow and deeper groundwater;
- the metal loads of the surface water drainage network.

This paper focuses on the Beekloop-Keersop, Bulder Aa and Tungelroijsche Beek catchment. The approach (Fig. 2) started with a spatial reconstruction of the historic atmospheric deposition followed by an unsaturated zone transport model to calculate metal leaching to groundwater. Agriculture and other sources of heavy metals were also

taken into account. After this, a 3-dimensional reactive transport model was used for the saturated zone. Calculated and measured concentrations were compared for validation of the modeling.

2. ATMOSPHERIC DEPOSITION AND UNSATURATED ZONE TRANSPORT

Leaching of cadmium and zinc from topsoil to groundwater in the Kempen area is spatially highly variable. It depends on the soil type, the groundwater depth and input load of the metals by atmospheric deposition and agriculture. The unsaturated zone model HYDRUS-1D (Šimůnek et al., 1998) was used to model the leaching of cadmium and zinc to the groundwater in the period 1880-2005. Non-linear Freundlich adsorption isotherm coefficients (K_F) were derived from an existing multiple linear regression model (Römkens el al., 2002):

$$\log [Q_{Cd}/C_{Cd}^{0,54}] = -5.01 + 0,27 \log [\% \text{ clay}] + 0,65 \log [\% \text{ SOM}] + 0,29 \text{ pH} \quad (1)$$

where Q_{cd} is the cadmium content in soil (mol/kg), C_{Cd} is the cadmium concentration in the soil solution (mol/m^3) and pH the acidity of the soil (0.01 M $CaCl_2$).

Input parameters for the regression model (pH, organic matter, and clay content) were taken from the chemical characterization of soil types from the Dutch soil map (De Vries, 1999). Together with the groundwater level the sorption of metal determines the breakthrough time to the groundwater. Groundwater levels were derived from a regional groundwater flow model. The Van Genuchten parameters for modeling the unsaturated water flow were calculated with pedo-transfer functions from soil parameters like texture, bulk-density and organic matter content (Wösten et al., 2001). A precipitation excess of 300 mm/year was used for the model.

No temporal or spatial data about the (historic) atmospheric deposition of the metals covering the total Kempen region is available. Therefore, the atmospheric deposition of the metals was reconstructed from the analyzed cadmium content in 19 forest soil samples. Forest soil samples were chosen because the metal contents in these soils are not influenced by agricultural activities.

At the 19 locations with varying distances from the smelters, the historic atmospheric deposition of the metals was reconstructed by inverse modeling with the analyzed cadmium content in the soil, using HYDRUS-1D. Non-linear Freundlich adsorption isotherm coefficients (K_F) were derived from analyzed pH, organic matter and clay content of the samples (1).

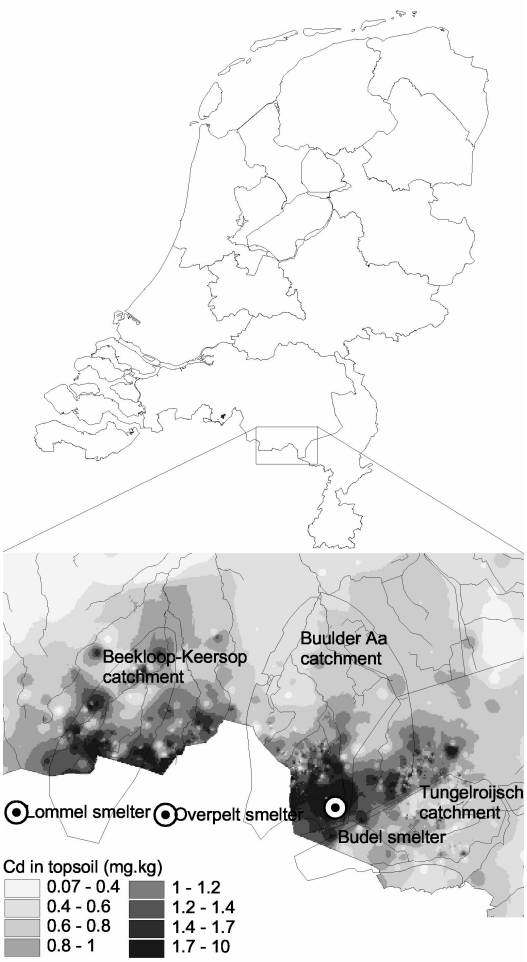

Figure 1. Map showing the location of the Kempen area in the Netherlands, the Beekloop-Keersop, Buulder Aa and Tungelroijsche Beek watershed and the cadmium amount in the topsoil for the year 1995.

The results indicate that the historic atmospheric deposition of the metals decreases strongly with the distance from the zinc smelters. For cadmium, the modeled average atmospheric deposition at the 19 locations in the period 1880-1975 vary between 15 and 642 g/ha/yr depending on the distance from the smelters. For zinc the levels varies between 730 and 25000 g/ha/yr.

The calculated deposition at the 19 locations was spatially interpolated to an area-covering map of atmospheric deposition rates. The distance from the smelters and the predominant wind direction are input variables for the interpolation.

Breakthrough curves of the metals were calculated for all unique combinations of soil type, groundwater level, input load and land use in the area. In total there were 16720 unique combinations. The agricultural load was determined by data about municipal and national use of manure and fertilizer salts respectively. The data were combined with other data like composition of manure to calculate the historic cadmium load by agricultural activi-

ties. Agriculture and other sources of heavy metals are small compared to the historic atmospheric deposition in the vicinity of the smelters. The average agricultural cadmium load was 1.48 g/ha/yr and zinc 605 g/ha/yr.

3. SATURATED ZONE

The results of the unsaturated zone model were used as recharge concentrations for the saturated zone model. The output of the unsaturated zone was averaged per 5 years to match input for the groundwater transport model. For the period from 1950 to 2005 the transport of cadmium in groundwater was calculated. The saturated zone model set-up was based on a MODFLOW finite difference groundwater flow model (McDonald & Harbaugh, 1988) and a MT3DMS transport model (Zheng & Wang, 1999) (Fig. 2). The grid discretization of the model is 100 meters horizontal and vertically varying 3 meters for the upper 5 layers to about 15 meters for the deeper layers in order to minimize numerical dispersion. The Buulder Aa catchment groundwater model encompassing an area of 24 x 17.5 kilometers contains 546000 model cells.

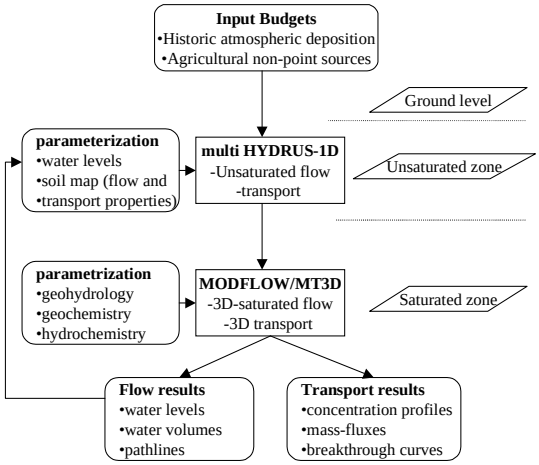

Figure 2. Structure of the integrated modeling system

3.1 Reactive transport

Sorption of cadmium was described in each individual model cell by pH-dependent single-solute Freundlich isotherms (Griffioen et al., 1998). These were calculated in three steps. First the activity of the free cadmium was calculated from the total dissolved concentration taking into account the major inorganic aqueous complexes and complexation with dissolved organic acids, including competition of Ca, Mg, Fe, Al and other trace metals. Data about the groundwater composition was obtained from 370 groundwater analyses from regional groundwater quality monitoring networks (Broers, 2002). Averages of concentrations were derived per so-called homogeneous areas for groundwater composition. Areal zones were considered to be homogenous regarding groundwater quality based on sampling from land use/soil-type/geohydrology strata. The variation in groundwater composition between those areas was expected to be larger between those areas than within them.

These homogeneous areas are created by overlay of four depth intervals (0-6, 6-15 and 15-35 and >35 meter beneath the groundwater level), two land use functions (agricultural and nature) and three geohydrological regimes (recharge, intermediate and discharge).

Second, the calculated activity of the free ion was used to calculate the related sorbed amount for individual sorbents present. We consider three types of sorbents and assume that the sorption to the three individual sorbents is additive (Griffioen et al., 1998). The three sorbents are clay minerals, iron oxides and organic matter. Third, the total sorbed amount was calculated as the sum of the products of the fraction sorbed and the amount of sorbents present:

$$S_{Cd} = S_{clay}\beta_{Cd,clay} + S_{ox}\beta_{Cd,ox} + S_{OM}\beta_{Cd,OM} \qquad (2)$$

where S_i refers to the amount of sorbent present and β_{Cd} is the fraction of the sorbent occupied with Cd. Data about the sorbent contents were obtained from 327 sediment analyses from 16 drillings in the area. Analyses were averaged per geological unit and isotherm functions per geological unit were calculated for these averages. The Freundlich isotherm that is used in the groundwater transport model was obtained from an empirical fit of the total sorbed amount versus the total concentration.

4. MODEL VALIDATION AND PREDICTION

4.1 Validation

Validation of the model was done by comparison of measured and modeled cadmium concentrations. Two data sets with measured cadmium concentrations of the upper meter groundwater were available: one with 1990 data and one with 2002 data. The 1990 and 2002 dataset contains 44 and 47 samples respectively in the three catchment areas (Fig. 1). Both were sampled with temporarily installed observation wells. The concentrations at the single locations are compared with the calculated concentration in the corresponding 100 x 100

meter grid cell. The concentrations are plotted against each other in Fig. 3.

An increase in measured and modeled concentrations is observed from 1990 to 2002. There is large scatter in the data. Figure 4 presents boxplots of the measured and calculated cadmium concentration in 1990 and 2002. A comparison reveals that the median and range of the values are in the same order of magnitude. However, for individual locations concentrations can differ by 2 orders of magnitude. This difference for individual locations cannot be explained.

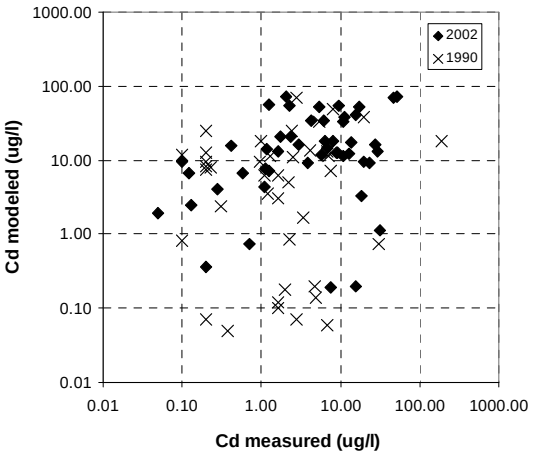

Figure 3. Measured and modeled cadmium concentrations (µg/l) in the upper meter of groundwater in 1990 and 2002.

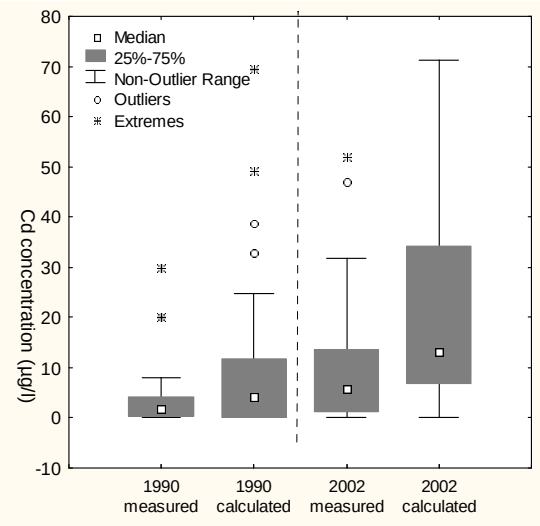

Figure 4. Boxplots of measured and modeled cadmium concentrations (µg/l) in 1990 and 2002.

4.2 Results

Table 1 gives the cumulative mass budgets for cadmium and zinc of the Beekloop-Keersop, Buulder Aa and Tungelroijsche Beek catchments. The calculated ratio between zinc and cadmium changes in time. From 1990 to 2005 the Zn:Cd ratio of the leaching water decrease from 137 to 112. The same is observed in the analyzed groundwater samples. In 1990 the average ratio of the shallow groundwater samples was 133 and in 2002 it was 118. The measured and calculated ratios are comparable despite the total different way in which they were derived. The shift in Zn:Cd ratio in time is a result of a slightly higher mobility of zinc over cadmium.

Table 1. Calculated cumulative mass budgets for cadmium and zinc of the Beekloop-Keersop, Buulder Aa and Tungelroijsche Beek catchment (1000 kg).

	unsaturated zone	saturated zone		discharge surface water
	leaching	Solute	Sorbed	
Beekloop-Keersop				
Cd 1990	3.2	0.6	2.1	0.6
Cd 2005	8.5	1.2	5.8	1.5
Cd 2050	19.6	1.7	12.3	5.6
Zn 1990	620	88	396	142
Zn 2005	1085	135	680	275
Zn 2050	2152	194	1247	714
Buulder Aa				
Cd 1990	14.3	3.5	9.5	1.3
Cd 2005	27.5	4.5	19.7	3.3
Cd 2050	53.5	5.8	36.4	11.2
Zn 1990	1796	390	1169	243
Zn 2005	2789	431	1940	422
Zn 2050	4899	458	3356	1088
Tungelroijsche Beek				
Cd 1990	6.1	1.3	3.4	1.4
Cd 2005	10.4	1.3	6.3	2.8
Cd 2050	23.2	2.2	11.4	9.7
Zn 1990	813	120	475	218
Zn 2005	1304	116	778	410
Zn 2050	2750	121	1264	1365

The results indicate a difference between the areas. For Beekloop-Keersop the amount of cadmium leached to the groundwater increases more than a factor 2.6 in the period between 1990 and 2005. For Buulder Aa the factor is almost 2 and for Tungelroijsche Beek the factor is 1.7. The soils in the Beekloop-Keersop area are more vulnerable for leaching than in the Tungelroijsche Beek catchment. For zinc, the difference between the different catchments is less obvious.

In the saturated zone in all areas the cadmium becomes strongly retarded, despite the low reactivity of the sandy sediments. In 2005 about 10% of the leached cadmium will have been discharged in seepage areas.
Figure 5 gives the simulated cadmium load by subsurface outflow of groundwater to surface water in the Beekloop-Keersop and Tungelroijsche Beek catchment as flux in kg/year and concentration in µg/l. The concentrations were calculated from the cadmium and water flux without considering geochemical processes in the stream sediment. Due to anaerobic conditions precipitation of metal sulfides in this sludge is likely, the stream sediment then acts as a sink for cadmium and zinc.

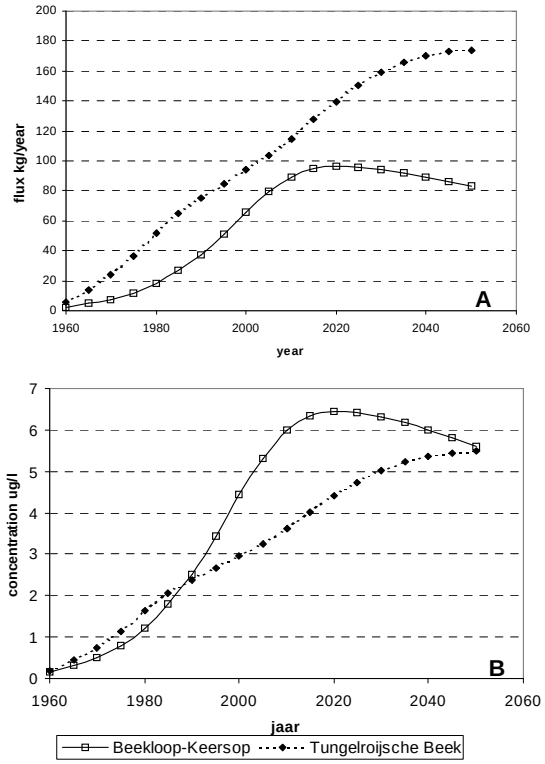

Figure 5: Simulation of cadmium load by seepage of groundwater to surface waters in Beekloop-Keersop and Tungelroijsche Beek catchments, (A) flux in kg/year and (B) concentration in µg/l.

The modeled concentrations of the surface water by seepage in both catchments are in the same range of several µg/l and will increase for the next decades. This simulation shows that for the Beekloop-Keersop catchment a peak will be reached in the period 2015-2020. For Tungelroijsche Beek the flux and concentration will increase until 2050.
Regarding leaching of solutes from groundwater to surface water, the results of the reactive transport simulation are opposite to results of conservative (non-reactive) transport that was modeled as well. For a non-reactive tracer, the Tungelroijsche Beek is the quickest responding system, whereas reactive transport modeling shows that the Beekloop-Keersop is the quickest. This turn round of quicker hydrological system to slower hydrochemical system and vise versa is caused by a difference in soil type between the areas. The soils in Beekloop-Keersop are more vulnerable for leaching of metals than the soils in of Tungelroijsche Beek catchment.

4.3 Uncertainty

A small amount of data was available for parameterization of the historic atmospheric deposition of cadmium and the reactivity of the sediments. These parameters are the input terms of the model with the most uncertainty. However, a comprehensive sensitivity analysis was not performed. Preliminary results indicated that the model is sensitive for the net precipitation excess and the pH of the groundwater. The net precipitation excess determines the flow-rate of the groundwater and varies between 150 and 500 mm/year mainly dependent on the land use. The pH is predominating in the retardation of cadmium and varies between 4.5 and 7.

5. CONCLUSIONS

The integrated modeling approach with coupled unsaturated flow and transport plus a saturated groundwater flow and transport model predicts average cadmium concentrations in the shallow groundwater that are in the same order of magnitude and have the same range in concentrations as measured values. However, for individual locations concentrations can differ by 2 orders of magnitude. The Zn:Cd ratio of the modeled values and measured samples are well comparable despite the independent way in which they were derived.
The coupled model enables the generation of credible and acceptable information. The coupled model can be used to run future scenarios with different measures to reduce the cadmium problem in the Kempen area. The information generated by the model is suitable for support in the decision making and planning process in the area. A precondition for this is that the uncertainties in input parameters and the model approach are made clear to all parties involved in the decision making and planning process.

6. ACKNOWLEDGEMENTS

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