Contribution of agriculture to the heavy metal loads of Dutch surface waters

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Abstract Heavy metals in surface water originate from direct inputs (wastewater treatments, industry) but also from nonpoint sources including the contribution from groundwater and, initially leaching from soils to groundwater. The magnitude of the pathway soil \(\rightarrow\) groundwater \(\rightarrow\) surface water, however, remains largely unknown but is believed to be quite substantial for elements like Cd, Cu and Zn. In this paper a method is described for obtaining a first estimate of the magnitude of the contribution of metal leaching from soil to the load in surface waters, although precise estimates are difficult to obtain due to the lack of data and variability in soil properties. Current estimates are based on measured data from lysimeter studies and mass balance approaches, and range from 34% for Cu to 59% for Cd. A framework that is currently being developed is discussed and will eventually be used to obtain more reliable estimates.

Key words agriculture; groundwater; heavy metals; leaching; soil; surface water; The Netherlands

INTRODUCTION

Until quite recently the contribution of heavy metal leaching from arable soils and natural land to surface waters in The Netherlands was considered to be negligible compared to other sources. However, the contribution of many (point) sources (e.g. industry, traffic) has decreased considerably during the last decades and it may well be possible that metal leaching from soil to surface water significantly contributes to the total metal load in surface waters. In areas with more pronounced topographic differences (hilly and mountainous areas etc.), the contribution of surface runoff and erosion can also be significant but in The Netherlands (with the exception of the hilly areas in the southern parts of the Province of Limburg), this contribution is considered to be of less importance. Recent estimates of the International Rhine Committee (IRC, 1996) indeed do suggest that metal leaching from soil has become a significant source for metals in surface waters. These estimates have resulted in a proposal to study metal leaching from soils to surface waters in rural areas (leaching from urban areas is not considered). A literature search was conducted to collect data on dissolved metal concentrations in surface waters and groundwater. Also, RIZA has started a campaign to measure metal concentrations in surface water and groundwater in a selected number of regions throughout The Netherlands; results are currently being collected. A theoretical framework is being developed to estimate the metal flux from soils to...
surface waters. This framework is to be used to estimate the contribution of metal leaching from (surface) soils to the upper groundwater and from there to surface waters and includes input through both subsurface runoff and deep groundwater.

IRC ESTIMATES OF METAL LEACHING FROM ARABLE SOILS

IRC (1996) distinguished four different flowpaths that contribute to the total load in surface waters as a result of agricultural activities: (a) direct emissions, (b) erosion, (c) runoff, and (d) leaching. According to the results from the IRC study, metal leaching from soil is the most important contributor to the total load and ranges from 60% for Cr to 98% for Cd. These estimates were obtained by multiplication of the measured concentrations in drainage pipes and the amount of water that drains from these drains into the River Rhine, which is equal approximately to 855 000 m$^3$ year$^{-1}$ for The Netherlands. The concentrations used to obtain the total load were measured in Germany and were 5 µg l$^{-1}$ for Cd, 15 µg l$^{-1}$ for Cu, 200 µg l$^{-1}$ for Zn, 15 µg l$^{-1}$ for Pb, 3 µg l$^{-1}$ for Cr, and 10 µg l$^{-1}$ for Ni.

In the Annual Report on Emissions and Wastes (Ministry of VROM, 1999) an overview of all emissions of heavy metals to surface waters is published each year. If we compare these emissions with the estimated metal flux from arable soils to surface waters as reported by the IRC for The Netherlands, the contribution of leaching seems to be highly significant and ranges from approximately 10% for Pb, 20% for Cu, 30% for Zn, to almost 60% for Cd.

DISSOLVED METAL CONCENTRATIONS IN SURFACE WATERS

The quality of surface waters has improved steadily since 1985 (CIW, 1998). In 1996, the average dissolved Cu concentration in regional surface waters was, however, still approximately two times higher than the maximum tolerable concentration (MTR). For Zn, the average concentration decreased to approximately 1.1 times the MTR value. In large rivers like the Rhine, Meuse and IJssel, water quality has also improved but average dissolved metal concentrations still exceed the MTR; in 1997 the average Cu and Zn concentration was still 1.7 and 1.3 times the MTR respectively. However, in certain cases, heavy metals are still a problem in surface waters and an inventory from 1996 shows that water quality in certain regional water systems sometimes is poor (CIW-CUWVO, 1996). The inventory contains a map that shows all locations where the MTR for Cd, Hg, Cu, Ni, Pb, Zn or Cr is exceeded. At a large proportion of the sampling points, at least one of the metals exceeds the MTR, and at a substantial number, the ratio between the actual concentration in the surface waters and the MTR is higher than 5.

AVAILABILITY OF DATA TO ASSESS HEAVY METAL LEACHING

Data that enable us to accurately estimate metal leaching from soils are scarce. In 1991 and 1997 results from a lysimeter study were published that include measurements of
Fig. 1 Estimated concentration of Cu in drain water according to the IRC and measured concentrations in various lysimeter studies and groundwater.

Cd, Cu, Zn, Pb and Ni solution concentrations in leachates from clay- and sandy soils (Van Erp & Van Lunc, 1992; Westhoek et al., 1997). Based on these data, the estimates of the IRC on Cd, Zn and Pb leaching fluxes seem to be rather high, but for Cu reasonable estimates were obtained. However, the data for 1992 were obtained in lysimeters and still do not reflect conditions and variability in "real" field sites. The National Institute for Health and the Environment (RIVM) has established a monitoring network on the quality of the upper groundwater (Van Swinderen et al., 1996). Concentrations were measured in the upper groundwater (0–5 m below the surface) on farms throughout The Netherlands. Measured concentrations for Zn and Cu are in good agreement with data from the IRC but measured concentrations for Cd were substantially lower in the RIVM network compared to the IRC estimates. However, regional differences can be substantial as was observed in a study of the quality of the upper groundwater in the south of The Netherlands (Province of Limburg; Karssemeejer et al., 1991). Measured heavy metal concentrations exceed those obtained by RIVM and range from 2.1 μg l⁻¹ for Cd and Pb, to 20.7 μg l⁻¹ for Cu, to 560 μg l⁻¹ for Zn. However, the elevated Cd and Zn concentrations are possibly related to the presence of a smelter that is known to have had a significant impact on the amount of Cd and Zn in soils in the vicinity of various sampling points. Figure 1 shows the estimates for Cu obtained by the IRC as well as the results from the lysimeter studies and measurements on the quality of groundwater. Current Dutch background level (achtergrondwaarde), target values (streefwaarde) and MTR (maximum tolerable risk level) values for groundwater and surface water are also given. For most samples, measured values for Cu in groundwater are more or less equal to the target value for groundwater. However, if no further reduction of the Cu concentrations occurs during subsurface runoff or transport through deep groundwater, concentrations in surface waters will exceed current target values. Comparison of
measured concentrations with MTR levels in surface waters shows that for Cu, the MTR is exceeded by a factor of 2 to 4 in groundwater samples, to 6 in lysimeter studies. For Cd all measured concentrations are in between the target value and the MTR. For Zn, however, measured concentrations in groundwater also exceed both target values and current MTR levels (by up to a factor of 5).

**ESTIMATION OF LEACHING RATES**

In a study that was aimed to evaluate heavy metal mass balances at the farm scale, all inputs (e.g. manure, food) and outputs (e.g. leaching, crop uptake) were quantified (Moolenaar, 1998). Leaching rates were calculated as the rate at which metals are removed from the topsoil (0–30 cm) by water flow. This flux, calculated as the product of the water flux in a time period and the average dissolved metal concentration is, however, not necessarily equal to the amount of metals that, ultimately, leaves the soil by drainage. Leaching fluxes were either based on model calculations using sorption models and site-specific soil properties, or on measured or estimated dissolved metal concentrations. Leaching fluxes ranged from 0.5 to 2.8 g ha⁻¹ year⁻¹ for Cd, from 5 to 87 g ha⁻¹ year⁻¹ for Cu, from 4 to 35 g ha⁻¹ year⁻¹ for Pb, and from 2.6 to 88 g ha⁻¹ year⁻¹ for Zn respectively. The wide range in potential leaching fluxes already indicates that estimates based on these data result in a large degree of uncertainty. Despite these limitations, the data were used to calculate the total metal load due to leaching. To do so, we used the total area of arable land given in the IRC report (approximately 500,000 ha). We then compared the calculated leaching flux with data from the IRC report. Estimated leaching fluxes for Cd, Cu and Pb match those of the IRC, although the Zn flux seems to be too high.

One of the factors that contribute to variability in leaching fluxes is soil heterogeneity. A study by Boekhold (1992) showed that Cd leaching in the vicinity of a smelter ranged from 0 to 51 g ha⁻¹ year⁻¹ as a result of heterogeneity in soil properties (organic matter, pH, soil Cd content). The soil Cd content in this area is, however, substantially higher than in non-polluted areas, which results in high leaching fluxes, but the range in leaching fluxes due to heterogeneity is most likely equal to that of non-polluted soils.

**ESTIMATION OF HEAVY METAL LEACHING FROM ARABLE SOILS TO SURFACE WATERS**

Based on the data shown previously, the contribution of arable soils to the total metal load in surface waters was calculated using the IRC approach (Table 1). Data on land use (area) were obtained from the National Bureau of Statistics and data on concentrations in (upper) groundwater were obtained from RIVM (Van Swinderen et al., 1996). It was assumed that these concentrations are equal to those that ultimately reach the surface waters after transport through the aquifer.

In the calculations it was assumed that the concentrations measured at the farm scale equal the average concentrations for various land use types (arable land, grassland and horticulture). Despite the inherently crude nature of the estimate, the contribution
TABLE 1 Total metal leaching in 1996 and contribution of agriculture to total metal load in surface waters in The Netherlands.

<table>
<thead>
<tr>
<th>Flux (t year⁻¹):</th>
<th>Load from agriculture</th>
<th>Total emissions in 1996*</th>
<th>Contribution of agriculture (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>1.6</td>
<td>1.13</td>
<td>59</td>
</tr>
<tr>
<td>Cu</td>
<td>35.6</td>
<td>68.3</td>
<td>34</td>
</tr>
<tr>
<td>Zn</td>
<td>316</td>
<td>476</td>
<td>40</td>
</tr>
</tbody>
</table>

* Without agriculture.

of agriculture can be quite significant. Factors that will reduce the percentages shown in Table 1 include retardation during groundwater flow (although subsurface runoff can be rather quick) and immobilization (formation of metal sulphides) as a result of changing redox conditions in the aquifer.

RESULTS OF THE NEW SAMPLING PROGRAMME REGGE AND DINKEL

Preliminary results from the monitoring programme confirm various conclusions based on general data (Anonymous, 2000). Between 20 and 60% of all surface water samples exceeded MTR levels for Cu and Ni. Concentrations of Cu and Ni in groundwater are comparable to those mentioned previously and range from 10 to 20 µg l⁻¹ for Cu, to 20 to 60 µg l⁻¹ for Ni. For Zn, measured concentrations were lower than those used by the IRC and ranged from 20 to 50 µg l⁻¹. Dissolved metal concentrations in groundwater decreased with depth; concentrations in the samples taken from 5 m below the surface were lower than those taken at 3 m below the surface. This confirms that adsorption and/or redox processes significantly reduce the flux that leaches from the soil. Often the concentration in samples taken at 5 m below the surface were lower than those measured in the surface waters adjacent to the sampling points for groundwater. This suggests that lateral subsurface runoff indeed does occur which could contribute significantly to the total load of metals in surface waters.

A FRAMEWORK TO ASSESS THE IMPORTANCE OF METAL LEACHING FROM SOILS

The method used by IRC resulted in crude estimates of the leaching flux and its contribution to the load of heavy metals in surface waters. In this method only arable soils were included but it is likely that leaching from acid forest soils can be quite significant as well for metals like Cd and Zn. Furthermore the role of immobilization in the aquifer, due to adsorption or metal sulphide formation, has not been accounted for which could result in a significant decrease of the load during transport in the aquifer. Therefore, a new project has been initiated to takes into account both limitations and to derive a conceptual framework that can be used to estimate metal leaching from soils. Metal leaching from soils will be calculated using a recently developed model that takes into account sorption and complexation in the soil solution. The total leaching flux is calculated based on the average water table in the soil. This will result in a potential leaching flux that can be compared to the total load in surface waters. The total water flux that leaves the soil
profile is subsequently divided into a subsurface runoff flux and a flux towards the deep groundwater. As indicated by the data from the new monitoring study in the Regge and Dinkel area, the subsurface runoff is likely to contribute to the surface water quality, whereas the flux in the deep groundwater will have very large retention times in combination with redox related immobilization processes. The results are then lumped for various major land use types and soil types to identify which combination is prone to metal leaching (e.g., intensive cattle breeding on acid sandy soils). Preliminary model calculations for Cd are in good agreement with measured data on Cd in groundwater. The results indicate that—in acidic sandy soils especially—metal leaching is substantial and the flux from soils to groundwater is high enough to eventually contribute to the Cd load in nearby surface waters. However, before drawing conclusions, further model validation, taking account of measured data on ground- and surface water composition, still needs to be done.

CONCLUSIONS

Despite the improvement of the surface water quality in various major rivers during recent years, MTR levels are exceeded frequently in regional waters. Leaching from arable soils could be a potential source of heavy metals. The magnitude of this load, however, has not been determined in detail yet, and the role of agriculture in relation to surface water quality for heavy metals remains unclear. A crude estimate indicates that this contribution could be as high as 60% but various important factors that control the magnitude of the leaching flux have not been included as yet. New monitoring programmes and the design of a theoretical framework that includes processes like adsorption in the aquifer as well as redox processes, are in progress though and can be used to evaluate the risk of metal leaching of metals from arable soils.

REFERENCES