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Pesticides and nitrate in groundwater and rainwater in the province of Limburg, The Netherlands

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Abstract The purpose of this study was to investigate the occurrence of high concentrations of pesticides and nitrate in groundwater and rainwater in the province of Limburg, The Netherlands. Eight wells were sampled, six in the north and two in the south, and analysed for a suite of pesticides and nitrate. Rainwater also was sampled and analysed from two locations. Triazines were detected in groundwater; atrazine and simazine exceeded the groundwater human-health standard of 100 ng l^{-1}. In rainwater, 13 of 23 pesticides were detected, of which several had high concentrations; e.g. atrazine (>200 ng l^{-1}). Two of the pesticides detected in rainwater (β+γ-HCH and atrazine) exceeded the groundwater standard. Seven pesticides in rainwater exceeded the Target value and three pesticides exceeded the Maximum Tolerable Risk value (DDT, heptachlor and heptachlorepoxide A), which are used as ecotoxicological standards in The Netherlands. For atrazine in rainwater, exceedance of the TDI (Tolerable Daily Intake) level of 0.5 μg kg^{-1} day^{-1} was observed using the model HESP. Groundwater nitrate concentrations regularly exceeded the standard of 50 mg l^{-1}.

Key words groundwater; groundwater and ecotoxicological standards; nitrate; pesticides; rainwater; risk evaluation; The Netherlands

INTRODUCTION

In the province of Limburg, The Netherlands, one task of the Law Enforcement Section of the Department of Environment and Water, is to care for the environment. Investigations of the environmental quality of air, soil and (ground)water are conducted. This study was performed as a collaborative project involving the province of Limburg, the Department of Health Risk Analysis and Toxicology of the Faculty of Health Sciences of the University of Maastricht, and the Directorate-General of Public Works and Water Management, Directorate Limburg, Maastricht, The Netherlands. The main objectives of the study were to determine the occurrence of the most widely used pesticides in groundwater and rainwater in the province of Limburg, to determine the levels of exceedance of these pesticides using The Netherlands' groundwater and eco-toxicological standards, and to determine the human health risks of the occurrence of these pesticides.

The study area is in the southern part of the province of Limburg, the Central Plateau (Schimmert Plateau). The Central Plateau is an agricultural area of nearly 6000 ha. It is centrally located within the triangle of the industrialized and urbanized areas of Maastricht, Heerlen and Geleen. Land use is half grassland and half arable. The main crops are winter wheat (*Triticum* sp.), sugar beet (*Beta* sp.), and corn (*Zea* sp.). In addition, horticulture and fruit cultivation occur in some areas. The Maastricht-Aachen airport is located in the western part of the Central Plateau. The Central Plateau is a hydrogeologically closed system in that groundwater is recharged only by precipitation on the plateau and no lateral groundwater flow occurs with adjacent aquifers. Most of the annual average precipitation excess (~75%) is discharged from springs, i.e. phreatic groundwater. The Central Plateau is part of three catchments; the streams in the north discharge to the Geleenbeek, in the south to the Geul, and in the west to the Maas. The Geleenbeek and the Geul are tributaries of the River Maas. The relatively short residence time of the groundwater on the Central Plateau makes it a suitable area to study the relationship between pesticide use and groundwater composition.

METHODS

Sampling locations

Wells and natural springs Six locations were selected for the chemical analysis of groundwater collected from wells in the northern part of Limburg. The northern part of Limburg is dominated by sandy soils, which implies a high risk of pesticide leaching to groundwater. Two locations were selected for the chemical analysis of groundwater collected from wells in the southern part of Limburg. The southern part of Limburg is dominated by loess soils, which implies a low risk of pesticide leaching; two locations were selected here for analysis of groundwater in wells. Also, samples from 16 natural springs on the Central Plateau in the southern part of Limburg were analysed for pesticides and nitrate.

Rainwater Rainwater was sampled at two locations, one in the southern part of Limburg (Maastricht) and one in the northern part (Ysselsteyn). The sampling was conducted in June, August, September, October and November 1998, and January, March and May 1999. Animal farming dominates around Ysselsteyn, an agricultural area where maize, vegetables and cereals are grown, and animal farming occurs. The second rain sampler is located in Maastricht, on the roof of the government building (10 m above ground level). Pesticide use is restricted in Maastricht but is typical for farming areas in Ysselsteyn.

Analysis by gas chromatography

The water samples were concentrated and filtered by solid phase extraction (SPE). Apolar pesticides were analysed by gas chromatography-mass spectrometry (GC). For the SPE, 500 ml of sample was passed over a C18-SPE filter. The filter was eluted

with 1 ml acetone and 8 ml hexane. The solution was evaporated at room temperature to 1 ml. From this solution 25 µl was injected onto the GC-column (26.5 m CP Sil 8, 0.2 mm diameter, 0.11 µm layer). The gas chromatograph was a HP 6890, provided with a HP 5973 MSD (Mass Selective Detector, EI-SIM mode). The recovery of the pesticides by the GC method was about 70%, except for atrazine (30%) and simazine (15%). Results were corrected for recovery. The determination limits of the GC analyses were determined by the 10% RSD level of the analytical method, and are summarized in Table 1. This table also shows which pesticides were analysed by GC.

Table 1 Pesticide analytical detection limits.

Compound		Analytical detection limit (ng l^{-1})
Chloride pesticides	α-HCH	2
	β,γ-HCH	5
	δ-HCH	10
	Pentachlorobenzene	2
	Hexachlorobenzene	2
	Telodrin	5
	Isodrin	2
	Aldrin	5
	Dieldrin	2
	Endrin	10
	o,p'-DDE	2
	p,p'-DDE	20
	o,p'-DDD	2
	p,p'-DDD + o,p'-DDT	4
	p,p'-DDT	2
	Heptachlor	2
	Heptachloroepoxide A	2
	Endosulfan α	5
	Endosulfan β	5
Triazines	Simazine	10
	Atrazine	2
	Propazine	2
	Terbutryn	2

RESULTS AND DISCUSSION

Pesticides in groundwater

In one of the six wells from the northern part of Limburg, dieldrin was observed at a very low concentration (8 ng l^{-1}). In the two wells from the southern part of Limburg, atrazine was detected (12 and 93 ng l^{-1}, respectively), and in one well propazine at a concentration below the groundwater standard (3 ng l^{-1}). In the natural springs, pesticides from the group of triazines were detected: atrazine was detected in nine of the 16 springs, propazine in three springs, and simazine in one spring. Atrazine concentrations were above the groundwater standard of 100 ng l^{-1} in two springs (309 and 245 ng l^{-1}), and simazine in one spring (137 ng l^{-1}). The springs were also sampled

in previous years, and atrazine was detected. Nitrate concentrations in 15 of the 16 natural springs exceeded the groundwater standard of 50 mg l^{-1}; nitrate concentrations as high as 200 mg l^{-1} were measured.

Pesticides in rainwater

In the rainwater, 13 of the 23 analysed pesticides were detected in one or more of the samples: α-HCH, β+γ-HCH, δ-HCH, isodrin, dieldrin, p,p'-DDD + o,p'-DDT, p,p'-DDT, heptachlor, heptachlorepoxide A, endosulfan α, endosulfan β, atrazine, propazine. Most of these pesticides were detected at each location. δ-HCH and propazine were not detected at Maastricht and α-HCH and isodrin were not detected at Ysselsteyn. High concentrations of several pesticides were observed, e.g. atrazine (214 ng l^{-1}) and β+γ-hexachlorocyclohexane (β+γ-HCH, 142 ng l^{-1}). Atrazine and β+γ-HCH exceeded the groundwater standard of 100 ng l^{-1}. Rainwater nitrate concentrations of less than or equal to 5 mg l^{-1} were observed. The risk analysis was performed with the HESP model on exposure to pesticides due to deposition of rainwater and the use of groundwater for drinking. Atrazine exceeded the TDI (tolerable daily intake) value of 0.5 μg $kg^{-1}.day^{-1}$. An exposure value of 1.0 μg $kg^{-1}.day^{-1}$ was calculated for rainwater samples from Maastricht and 0.9 μg $kg^{-1}.day^{-1}$ for rainwater samples from the location Ysselsteyn. In The Netherlands, standards exist for surface water quality and are based on toxicological properties of compounds. The Maximum Tolerable Risk (MTR) value is based on the protection of humans and ecosystems for a short-term exposure (<1 year) to a concentration of a compound. The Target value is derived from the MTR, and it represents a negligible risk at long-term exposure (>5 years). The factors of maximum excess of the standards by pesticides found in rainwater are shown in Table 2. For rainwater, seven pesticides exceeded the Target value, and three pesticides exceeded the MTR value (DDT, heptachlor and in particular heptachloro-epoxide A).

Table 2 Maximum excess of standards by pesticides in rainwater.

Pesticide	Maximum excess of Target value Factor x	Maximum excess of MTR value Factor x
β+γ-HCH	16	
Dieldrin	8	
DDT		12
Heptachlor		8
Heptachloroepoxide A		18
Endosulfan α	80	
Atrazine	7	

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