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GROUNDWATER POLLUTION BY VOLATILE HALOGENATED HYDROCARBONS; SOURCES OF POLLUTION AND METHODS TO ESTIMATE THEIR RELEVANCE

T. TROUWBORST
Ministry of Health and Environmental Protection, The Netherlands;
Public Health Inspectorate.

ABSTRACT

An investigation was made of the prevalence of volatile halogenated hydrocrabons in groundwater used for production of drinkingwater in the Netherlands. In some cases concentrations of tri- and perchloroethylene were found at levels higher than 10 μg/l. In 50% of the groundwatersources these substances were detected at levels lower than 1 μg/l but higher than the detection limit of 0.01 μg/l, even in well protected areas. Cases with levels higher than 10 μg/l and probably 1 μg/l could be argued to be due to direct (point) discharges to the ground. From data of the Dutch emission inventory system it is calculated that air pollution may be the cause of groundwater-pollution at lower levels.

The emission inventory system allows sources of pollution to be classed by level of emission, industrial branche and type of installation, enabling a systematic identification of pollutants and their point sources.

INTRODUCTION

Recently an increasing number of reports have indicated that groundwatersources may be polluted by chemicals of industrial origin at places which were previously unsuspected. Especially the group of mobile, persistant low molecular weight halogenated hydrocarbons seemed to be one of the most prevailing categories of pollutants of groundwater.

In the Netherlands this type of pollution has received much attention after an accidental discovery in 1976 by the national institute of drinkingwater supply of the presence of trichloroethylene in drinkingwater prepared from a previously unsuspected groundwatersource. These findings underligned that commonly used routine chemical analyses of drinkingwater prepared from groundwater were inadequate to recognize this type of pollutants.

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Therefore the chief public health officer decided to initiate a national investigation of the occurrence of volatile halogenated hydrocarbons of all groundwatersources used for public drinkingwater supply. In this paper the results of this investigation are presented.

In the Netherlands about 50% of the drinkingwater is produced from groundwatersources and about 99,8% of the dwellings are connected to the public drinkingwater supply system. This means that most of the subtracted groundwater used for drinkingwater production is covered by this study.

METHODS

The samples were taken from subtracted groundwater behore treatment. Analyses were made by gaschromatography by the direct headspace method as well as by liquid extraction with a cyclohexane-diethylether mixture. Detection occured with an electron capture and a flame ionisation detector. At concentrations higher than 1 μg/l the measurements were repeated. The detection limit was 0.01 μg/l for tri- and perchloroethylene and 0.05 μg/l or less for other low molecular weight chlorinated hydrocarbons.

RESULTS

The investigation showed tri- and perchloroethylene to be the most prevailing pollutants in groundwater, with the exception of one single case of serious tribromoethene pollution in the vicinity of a past brominated products production site.

The results of the analyses show (fig. 1) that tri- and perchloroethylene were detected at levels higher than the detection limit of 0.01 μg/l in a high percentage of the samples.

Fig 1:

FREQUENCY DISTRIBUTION OF GROUNDWATERPUMPING-STATIONS ACCORDING TO CONCENTRATION OF TRI- AND PERCHLOROETHYLENE
DETECTION LIMIT: 0.01 μg/l
Data: HIMH

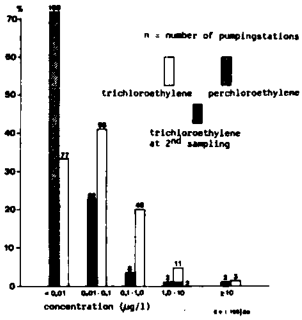


Table 1a

Emission of Trichloroethylene *

Province *	Number of registered sources emitting to air	Emission to air (ton/year)	Emission to water (ton/year)
Limburg (Z)	7	357	-
Z. Holland	99	359	-
N. Holland	61	343	15
Utrecht	20	82	-
Gelderland	49	166	-
Overijssel	24	62	2
Collective registration			
Dry-cleaning	1100	200	
aerosolspray	-	88	

* Data: Emission registration;The registration of the emissions in the remaining provinces has not yet been completed

In some instances concentrations were higher than 10 μg/l. These concentrations could be traced to past point discharges to the ground. In these cases measures had to be taken to reduce pollution of drinkingwater to an acceptable level.
In the region between 1 and 10 μg/l also a point source might be the cause of pollution. The concentrations below 1 μg/l could not be attributed to point sources, as they were also found in some natural well protected areas. At low levels analytical errors might play a role, but this alone does not explain the high frequency of concentrations at 0.1 - 1.0 μg/l, so that effects of diffuse (non-point) sources have to be taken into consideration.

EFFECT AND SOURCES OF POLLUTION. CALCULATED FROM EMISSION REGISTRATION DATA

Emission densities for important substances can be obtained from the Dutch system of emission inventory (EIS) which lists emissions to air and water.

The emission data are obtained by

a) individual registration (emission of pollutants from individual sources).
b) collective registration of specific categories of point-sources (obtained from number of point sources within each category and the specific emission for the point sources).
c) collective registration of non-point sources of pollution derived from human activities (f.i. pesticide use, pressurizing agents, traffic) and of natural origin (5).

The sources of emission can be classified according to industrial branche and type of installation. The emissions for tri- and perchloroethylene are given in table Ia, b for the registered provinces and the average emission density per province in table II. It appears that air emissions are predominant and that the emission density is high.

Table Ib

Emission of Perchloroethylene

Province *	Number of registered sources emitting to air	Emission to air (ton/year)	Emission to water (ton/year)
Limburg (Z)	11	165	-
Z. Holland	57	283	0,5
N. Holland	27	435	100
Utrecht	18	441	-
Gelderland	41	178	0,8
Overijssel	17	169	-
Collective registration			
Dry-cleaning	1100	5000	

Table 2

Emission density of Trichloroethylene

Province	Area (km^2)	Emission (air) of individual registered sources (ton/year)	Emission per m^2 (mg/year)
Limburg	2209	357	161
Z. Holland	3226	359	108
N. Holland	2912	343	118
Utrecht	1395	82	59
Gelderland	5131	166	32
Overijssel	3928	62	16

Collective registration	Emission	Emission factor
Dry-cleaning	200 ton/year	57 mg/inh. day
Aerosolspray	88 ton/year	25 mg/inh. day

A first approximation of the potential effect of air emission on groundwater quality can be obtained from emission densities (ca. 100 mg/m^2 year) and the annual rainfall data (precipitation: 750 mm per year). If it is assumed that all of the substances will be washed out and taken up in het rainwater, a concentration is calculated of 130 µg/l.

If we take into account the degradation, the rate determining step will be the degradation in the air with a half-life of about 6 weeks for trichloroethylene (1). In the (ground)water phase the half-life is many years.

Assuming a first order degradation, the disappearance rate will be:

$$\frac{dm}{dt} = - km_t = - \frac{\ln 2}{t_{½}} m_t$$

where $t_{½}$ is the half-life and m_t is the mass of trichloroethylene at time t.

In the "steady state" situation, the decrease due to degradation will be compensated for by the emission, which amounts to:

$$\frac{dm}{dt} = Q$$

At steady state: $m_t = \frac{t_{½} \times Q}{\ln 2}$

and it follows that at $t_{½}$ = 6 weeks: $m_t = 0.166 \times Q_j$ where Q_j is the emission per year. Provided that the mass of the substance in air is not much influenced by wash-out and rain-out, then degradation will reduce the maximum possible concentration in groundwater to 130 x 0.166 = 22 µg/l.

In practise also other factors like volatilization and dilution through aerial transport will play a role. The partition coëfficent of thrichloroethylene (2.74) suggests that indeed only a part of the substance in the air will be washed out.

Direct analyses of trichloroethylene in rainwater have shown concentrations of 0.15 - 1 µg/l (1,2), but data on concentrations in basins just after rainfall suggest that even concentrations up to 10 µg/l might be found (3).

From these data it may be concluded that the pollution of groundwater below 1 µg/l might stem from air pollution.

Industrial branches strategy

To abate and prevent pollution it is important to know the potential sources of pollution, their relative contribution to pollution and the most important industrial activities and branches.

From data of the emission inventory system a distribution of industrial branches to emission level per branche can be made (fig. 2). It appears that 90% of the emission (to the air) is causes by 24% of all trichloroethylene emitting branches. The most important industrial branches are given in table 3.

Fig. 2

DISTRIBUTION OF INDIVIDUAL REGISTERED TRICHLOROETHYLENE EMISSIONS

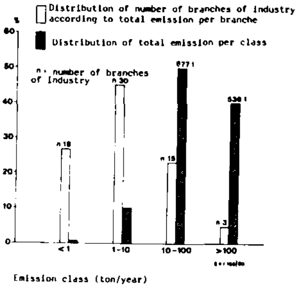


Table 3

Branches of industry listed according to decreasing emission level of trichloroethylene (Data: ERS)

Emission level (ton/year)	Branches of industry
296	Manufacture of paper and paper products
139	Manufacture of fabricated metal products, except machinery and transport equipment
102	Electrical enginering
95	Printing, publishing and allied industries
82	Laundries, chem. cleaning, dyeing etc.
73	Manufacture of artificial and synthetic filaments and staple fibres (except glass)
73	Manufacture of transport equipment
62	Blacksmith's workshop, grinding and surface treatment of metals, machinery and transport equipment
50	Manufacture of insulated wires and cables
42	Manufacture of screws, bolts, nuts and technical springs in mass production
36	Manufacture, assembly and repair of aircraft
33	Manufacture of other electrical apparatus, appliances and equipment n.i.c.

The emission inventory system allows a similar type of distribution to be made for emissions by individual installations (fig. 3). 69% of total air emission is caused by 9,4% of the emitting installations. The emission of the most important installations are presented in table 4 by name of their industrial branche.

Table 4

Individual registered emissions (> 30 t/y) of trichloroethylene from installations listed to level of emission

Emission t/y	Branche of industry
296,0	Manufacture of paper and paperproducts
90,5	Printing, publishing and allied industries
56,3	Manufacture of metal packaging
50,4	Manufacture of insulated wires and cables
50,4	Chemical cleaning
42,3	Mechanical engineering
40,3	Manufacture of artificial and synthetic filaments and staple fibres (except glass)
38,3	Manufacture of technical instruments

Table 6

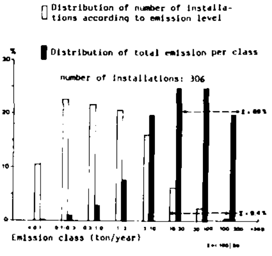
Registered chlorinated hydrocarbons emitted in quantities higher than 100 t/y in a single province in 1974 (Zuid-Holland)

Substance	air-emission (t/y)	Substance	air-emission (t/y)
Dichloromethane	3601	Trichloroethane	247
Dichloroethane,1,2 -	597	Trichloroethylene	369
Perchloroethylene	273	Vinylchloride	2341

A further classification of summed emission per type of installation and number of installations within each category is given in table 5. A similar type of classification for perchloroethylene has been presented elsewhere (4).

Fig. 3

DISTRIBUTION OF INDIVIDUAL REGISTERED TRICHLOROETHYLENE EMISSIONS



Data: Emission registration, The Netherlands

Table 5

Totalled emission per type of installation, listed to level of total emission per type, and the number of installations within each category. The emission of the installation with highest and lowest emission level are indicated.

Type of installation	Summed emission per type of installation (t/y)	Number of installations	Highest emission (t/y)	Lowest emission (t/y)
1. Cleaning, degreasing, staining, fosfatising, chrometising, passivating	806	163	56	,024
2. Production of paper bags	296	1		
3. Remaining printprocesses	91	1		
4. Chemical cleaning of cloths and other textiles	82	4	41	,050
5. Moulding of synthetics	45	4	40	1,462
6. Metal milling and turning	43	27	14	,060
7. Galvanising, dipping and other means to apply metallic layers	34	13	9	,016
8. Applying paints to metal	15	10	6	,011
A. Total number of installations (emission higher than 10 ton/y)	1.412	223		
B. Total of all tri-emitting installations	1.503	306		
C. A as percentage of B	94	73		

Other substances

The calculations have shown, that emission levels of 100 mg/m^2 per year may have an effect on the quality of groundwater. There are other substances with a comparable emission density. As an example registered emissions with levels higher than 100 tons/ year in an industrialized province are presented in table 6 for some halogenated hydrocarbons. Registration has taken place in this particular case in 1974. Measures for reduction have been taken thereafter, sothat the present-day situation may deviate.

Though final effect on groundwater quality will also depend on factors like adsorption, mobility and degradability these datamay give an impression of the order of magnitude of the background pollution. It may be expected that the registered emission levels are typical for industrialized areas, sothat these data may have a broader significance.

CONCLUSIONS

The reported cases of point source pollution have indicated the necessity to monitor the quality of groundwatersources routinely for the presence of the discussed classes of substances as is the present-day practise in the Netherlands. The first measure to be taken however remains protection of aquifers against (potential) point sources of pollution. This ultimately gives the best guarantee of drinkingwater quality.

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