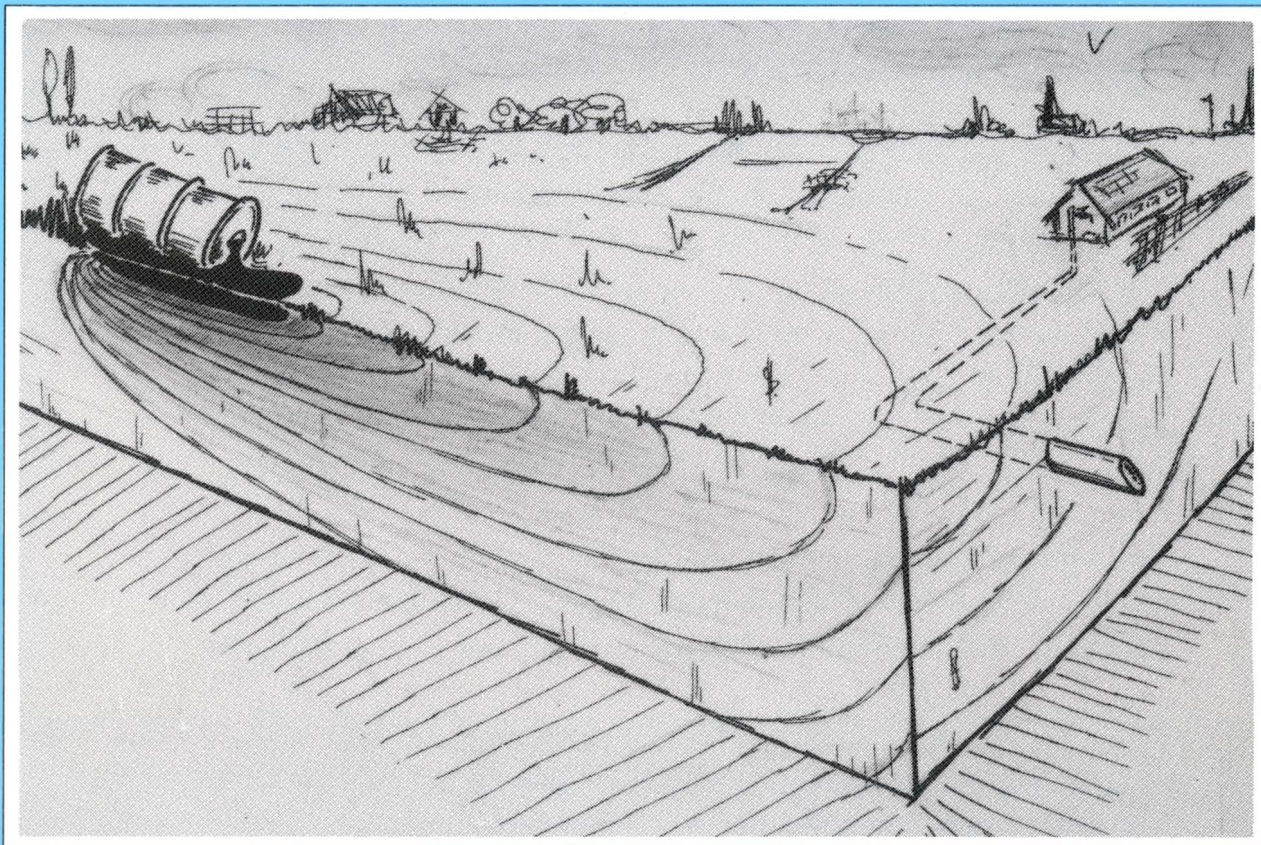# water lines in contaminated soil

EFFECTS OF SOIL CONTAMINANTS AND PIPING MATERIALS
ON DRINKING WATER QUALITY

A SUMMARY

.

Drs. G. Veenendaal

Ir. L.A.H.M. Verheijen

Dr. M.W. Vonk

KIWA N.V.

Nieuwegein, The Netherlands, October 1985

Keuringsinstituut voor Waterleidingartikelen
KIWA N.V.

Correspondence address:

Sir Winston Churchill-laan 273
Postal Box 70
2280 AB   RIJSWIJK
The Netherlands
Telephone (070) 95 35 35
Telex 32480
Postal Checking Account 52 92 95

Research Laboratory:
Groningenhaven 7
Postal Box 1072
3430 BB   NIEUWEGEIN
The Netherlands
Telephone (03402) 6 08 60

The research project, "The Effects of Soil Conta-
minants and Piping Material on Drinking Water
Quality", the results of which are summarized in
the present report, was started in 1981 at the
initiative of the former minister of Public Health
and Environmental Protection, now Housing, Physical
Planning and Environment (VROM), the Manufacturers
of Drinking Water Pipes made of Plastics, Asbestos-
Cement and Concrete and the Netherlands Waterworks
Association (VEWIN), which thus jointly financed
the investigation.

The project comprised two parts, namely, the trans-
port of organic compounds through the soil and the
permeation of organic compounds through piping
materials.

In order to perform the project in an acceptable
time interval, a number of limitations were imposed
from the beginning:
- the investigation was to be specifically directed
  toward the organic compounds which occur relativ-
  ely frequently as soil contaminants;
- the section on transport of organic compounds
  through the soil is limited to a critical review
  of the literature;
- the permeation study was directed toward piping
  materials which had KIWA marks of approval at the
  beginning of the study.

The investigation was brought to a close at the end
of 1984, with the exception of one part, namely,
the permeation of organic compounds through rubber
rings, which are used in couplings for drinking

water lines. This investigation is being continued at KIWA in 1985.

In KIWA Reports nos. 85, 86 and 87, the state of affairs with regard to the investigation is established.

Government and water supply companies can use this information as the basis for the formulation of policy regarding soil contaminations in the vicinity of drinking water lines and can offer industry a new aspect for consideration in the development of piping materials.

The Steering Group on Permeation

TABLE OF CONTENTS

.

1   INTRODUCTION

At the end of 1980, the public drinking water
supply in the Netherlands was confronted with
methylbromide in drinking water in the vicinity of
greenhouses. Methylbromide was used for disinfec-
ting the soil and was introduced into the soil as a
gas for that purpose. In this soil polyethylene
(PE) pipes had been laid at a shallow depth by the
owners of the greenhouses. As a consequence of this
incident KIWA carried out an investigation into the
permeation of methylbromide through PE and PVC
pipes.

The phenomenon of permeation, which implies the
penetration of compounds through the pipe wall
without causing this pipe to leak, was discovered
more than 25 years ago. Report no. 2 of KIWA from
1959, which was performed under contract with the
Commission on Plastic Water Supply Pipes, mentions
some incidents in which drinking water conveyed via
a PE service line was found to taste of natural gas
and gasoline. These lines were located in the imme-
diate vicinity of defective natural gas or gasoline
lines.
Since that time, at locations where it is known
that heavy contamination with organic compounds can
occur, for example, near gasoline service stations,
plastic water supply pipes have not been used.
Since the end of the 1970's, in the Netherlands,
however, a great number of locations have been
discovered where the soil is heavily contaminated
with organic compounds as a consequence of acci-
dents, dumping or intentional application of chemi-
cals (for example, pesticides). These contamina-
tions principally involve aromatic hydrocarbons

(benzene, toluene and the like), chlorinated al-
kenes (trichloro-ethylene and the like) and alkanes
(mineral oil).

The above, and the methylbromide affair, plus the
fact that a relatively large amount of plastic
water piping is used in the Netherlands (in 1981,
32 % of the main and distribution networks (50 mm
or more in diameter) consisted of PVC, i.e., ca.
27.000 km) induced the Ministry of Public Health
and Environmental Protection (as it was called at
that time), the Manufacturers of Water Supply Pipes
made of Plastic, Asbestos-Cement and Concrete, and
the VEWIN to commission a broad-scale study by KIWA
on the effect of soil contamination and piping
material on drinking water quality. The purpose of
this investigation was that of obtaining an under-
standing regarding the mobility of organic com-
pounds in the soil and the permeation through
piping materials of substances which affect drin-
king water quality. Therefore, the study consisted
of two principal parts: transport of substances
through the soil and permeation of organic matter
through piping materials.

A qualitative description of the transport of sub-
stances in the soil and the effect of various fac-
tors on this is presented in Section 10.

The investigation into the permeation of organic
materials through pipe walls was directed to those
piping materials which had received the KIWA mark
of approval and in which permeation cannot be ex-
cluded a priori. This involves the plastics PVC,
LDPE and HDPE, rubber rings used in couplings and
the materials which are somewhat porous, namely,

asbestos-cement and concrete.

In section 2 of this report, a general introduction is given to the theory of permeation. Then the different types of pipe material are discussed separately.

The first part involves plastics: polyethylene (section 3), PVC (section 4) and rubber rings (section 5). The techniques used in the investigation into the permeation of organic compounds through plastics are described in section 6. Asbestos-cement and concrete are discussed in sections 7 and 8, respectively.

The last sections of this report contain the conclusions from the investigation.

This report is a summary of Report No. 85 in which the theory of permeation, the experimental design and the results are discussed in detail, and Report No. 86, in which the transport of organic compounds through the soil is discussed in further detail. Relevant literature references are included in both reports.

2   BACKGROUND AND PRINCIPLES OF PERMEATION

Permeation is defined as the transport of substances through a wall (membrane, pipe wall) under the influence of a difference in concentration of the substances on the two sides of the wall.

In the case of polymers (plastics), the permeation proceeds in three phases:

1. the organic substance dissolves in the polymer on the outside;

2. the organic substance diffuses through the polymer;

3. the organic substance emerges from the polymer on the inside.

It is apparent from the above that permeation through plastics is not determined solely by diffusion but also by the degree to which the substance is soluble in the polymer, namely:

$$P = D \cdot K \qquad\qquad (2.1)$$

where: P = permeability coefficient (m·/day)
        D = diffusion coefficient (m^2/day)
        K = partition coefficient, i.e., the concentration in the polymer divided by the concentration outside of the polymer

The diffusion coefficient D of an organic substance in a polymer is principally determined by the rigidity of the polymer chains and the dimensions of the molecule (organic substance). For substances which do not attack the polymer (make it swell or soften), the diffusion can be described by the two diffusion laws of Fick.

The partition coefficient K is determined by the
degree of similarity between the organic substance
and the polymer. The affinity of an organic sub-
stance for a polymer is generally greater, the
closer together are the polarities of the organic
substance and the polymer.

Both the diffusion coefficient D and the partition
coefficient K are functions of the temperature. It
is generally true that permeation increases with
rising temperature.

If the diffusion can be described by Fick's laws,
permeation through a pipe wall take place in the
following manner. When a drinking water line comes
into contact with a soil contaminant, this contami-
nant will dissolve in the pipe wall and diffuse to-
ward the drinking water. However, it will take some
time before the contaminant reaches the drinking
water. The quantity of substances entering the
drinking water per unit time increases until the
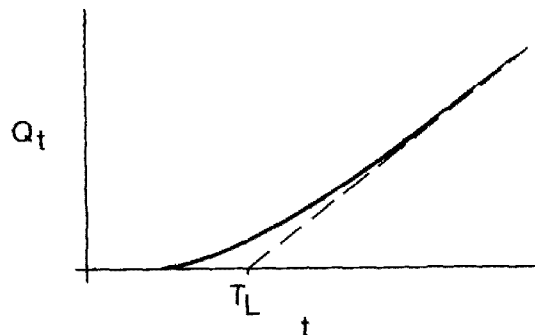steady state is achieved. This is shown in Fig.
2.1.

Fig. 2.1 - Permeation of an organic compound
through a drinking water line. When a
plastic drinking water line comes into
contact with a contaminant, the total
amount of organic compound (Q_t) which
has permeated through 1 m^2 of pipe wall
will increase over time according to the
above curve.

In the steady state, a constant amount of organic substance enters the drinking water per unit time. The asymptote intersects the time axis at the point T_L, the so-called time-lag intercept of Barrer and is given by:

$$T_L = \frac{d^2}{6D} \qquad (2.2)$$

where: T_L = time-lag intercept (day)
$\quad$ d $\;$ = wall thickness of the pipe (m)
$\quad$ D $\;$ = diffusion coefficient (m^2/day).

The theory described in the preceding is applicable for PE, PVC and rubber rings as long as there is no question of interaction between the organic substance and the plastic.

Asbestos-cement and concrete are somewhat porous materials, through which the drinking water penetrates to the outside under the influence of the water mains pressure. The organic substance must diffuse from the outside to the inside against this water flow. Since a theoretical description of this process is highly complex as a consequence of the material properties of concrete and asbestos-cement, the study on the permeation through asbestos-cement and concrete was, therefore, designed on a purely empirical basis.

3   POLYETHYLENE

3.1   General

The permeation of organic compounds through poly-
ethylene pipes can be described with the aid of the
two laws of Fick. This means that when the outside
of a pipe comes into contact with an organic conta-
mination, after a certain time, a constant amount
of organic substance enters the drinking water per
unit time (steady state).

The time t_s (days) elapsing between the first con-
tact with an organic contaminant and the attainment
of (96 % of) the steady state is determined by the
diffusion coefficient D (m^2/day) of the organic
compound and the wall thickness d (m) of the pipe.
The time t_s is given by:

$$t_s = \frac{d^2}{2D} \tag{3.1}$$

For all organic compounds investigated in the scope
of this study, in the case of an LDPE pipe with a
wall thickness of 3.5 mm, this time is between
approximately 60 days (chlorobenzene) and 400 days
(diphenyl).

The quantity of material which penetrates through a
pipe wall per unit time in the steady state is
determined by the permeability coefficient P, the
external concentration C_o and the dimensions of the
pipe. If the water flow in a pipe is stopped for
t days, the concentration C(t) in the drinking
water is:

$$C(t) = \frac{2 \cdot C_o \cdot t \cdot P}{r \cdot d} \tag{3.2}$$

where: $C(t)$ = concentration of the organic compound in the drinking water in the pipe after t days of standstill (g/liter);

C_o = concentration of the organic compound outside of the pipe (g/liter);

t = time during which the water has stood still in the pipe (day)

P = permeability coefficient (m^2/day);

r = internal radius of the pipe (m);

d = wall thickness of the pipe (m).

However, equation (3.2) is only applicable as long as it is true that:

$$C(t) << C_o$$

Since the permeability coefficient of an organic compound will differ for permeation from the vapor phase and the aqueous phase, in calculating the quantity of substance which permeated, a distinction should be made between the two situations (i.e., water and vapor). In addition, the permeability coefficient is often dependent upon the concentration. For example, for toluene, dissolved in water, the permeability coefficient P of toluene increases by a factor of 3 to 5 in the concentration interval of 100-300 mg/liter.

3.2   Permeation from groundwater

If the drinking water lines are below the groundwater table, the permeation will take place from the aqueous phase. The concentration in the aqueous phase can be established very accurately using current techniques. If the permeability coefficient is known, an estimate can be made of the quantity

of substance penetrating through an LDPE or HDPE
pipe in a given time with the aid of equation
(3.2).

For a number of compounds which have been investi-
gated by the, so-called, "flask" method (section
6), the permeability coefficients are known quite
accurately (Table 3.1).

For the substances which are comparable to the com-
pounds from Table 3.1, the same permeability coef-
ficient can be used as a first estimate. It is
apparent from this table that the aromatics inves-
tigated have permeability coefficients of 5.10^{-7}
(diphenylether) to 5.10^{-6} m^2/day (toluene). There-
fore, the conclusion appears justified that an
aromatic with one or several alkyl groups which
falls between toluene and diphenyl in terms of
size, will likewise, have a permeability coeffi-
cient on the order of 5.10^{-7} to 5.10^{-6} m^2/day. The
volatile chlorinated aliphatics, on the basis of
analogous reasoning to that for the aromatics,
should probably have permeability coefficients on
the order of 10^{-6} m^2/day.

For certain groups of substances, no permeability
coefficients are known and in addition, no esti-
mates can be made on the basis of correspondences
with the substances mentioned in Table 3.1 and/or
Table 3.2. For these substances, it is only
possible to make a very crude estimate on the basis
of liquid immersion experiments. Here, the maximal
value of the partition coefficient K is calculated
from the solubility S (which is determined from a
liquid immersion experiment) and multiplied by a
global estimate of the diffusion coefficient D.

In Appendix I, the values are presented for the solubility S of a large number of organic compounds in LDPE and HDPE. From this, the maximal values for the partition coefficient K_w can be calculated with the aid of equation (3.3):

$$K_w = \frac{S \cdot \rho}{C_w^{max}} \qquad (3.3)$$

with: S   = solubility of the organic compound in polyethylene (g/g);

ρ = density of polyethylene (g/liter);

C_w^{max} = maximal solubility of the organic compound in water (g/liter).

In Appendix I, the literature values for the maximal solubilities of C_w^{max} in water at 20 °C are also reported for a number of organic compounds.

The magnitude of the diffusion coefficient for small compounds is about 10^{-7} m^2/day and decreases with increasing size of the molecule (e.g., 2.10^{-8} m^2/day for diphenyl). With $P_w = K_w \cdot D$ in this manner, a very general estimate is obtained of the permeability coefficient. A comparison of the results of this estimation method with that of the "flask" method indicated that the estimate is higher, the more lipophilic are the substances.

In general, this estimate will also give a value that is too high.

Tables 3.1.a and 3.1.b also present, for given concentrations in the groundwater, the calculated concentrations of permeated material in the drinking water after 8 hr and 2 days of standing of the drinking water in an LDPE and HDPE pipe. It is apparent from these tables that the difference in the quantity of permeated material between an LDPE

LDPE

Organic compound	$P*.10^7$ (m^2/day)	$C_O = 10$ mg/liter		$C_O = 0,1$ mg/liter	
		t = 2 (day)	t = 0.333 (day)	t = 2 (day)	t = 0.333 (day)
toluene	12	1.10 mg/l	0.18 mg/l	11.0 µg/l	1.8 µg/l
diphenyl	4.8	0.44 mg/l	0.07 mg/l	4.4 µg/l	0.7 µg/l
diphenylether	5.0	0.46 mg/l	0.07 mg/l	4.6 µg/l	0.7 µg/l
trichloroethylene	16	1.46 mg/l	0.24 mg/l	14.6 µg/l	2.4 µg/l
tetrachloroethylene	7.7	0.71 mg/l	0.12 mg/l	7.1 µg/l	1.2 µg/l
chlorobenzene	35	3.20 mg/l	0.53 mg/l	32.0 µg/l	5.3 µg/l
1,3-dichlorobenzene	19	1.74 mg/l	0.29 mg/l	17.4 µg/l	2.9 µg/l
methylethylketone	0.058	0.005 mg/l	8.10^{-4} mg/l	< 0.1 µg/l	<0.1 µg/l
phenol	<0.0084	$<8.10^{-4}$ mg/l	$<1.10^{-4}$ mg/l	< 0.1 µg/l	<0.1 µg/l

Table 3.1.a - Calculated concentrations of permeated organic matter in the drinking water after 8 hr and 2 days of standing of the drinking water in an LDPE pipe (ϕ = 32 mm, wall thickness 3.5 mm). The concentrations in the groundwater (C_O) are 10 and 0.1 mg/liter, respectively.

HDPE

Organic compound	$P*.10^7$ (m^2/day)	$C_O = 10$ mg/liter		$C_O = 0,1$ mg/liter	
		t = 2 (day)	t = 0.333 (day)	t = 2 (day)	t = 0.333 (day)
trichloroethylene	7.2	1.03 mg/l	0.17 mg/l	10.3 µg/l	1.7 µg/l
tetrachloroethylene	3.8	0.54 mg/l	0.09 mg/l	5.4 µg/l	0.9 µg/l
chlorobenzene	19	2.71 mg/l	0.45 mg/l	27.1 µg/l	4.5 µg/l
1,3-dichlorobenzene	11	1.57 mg/l	0.26 mg/l	15.7 µg/l	2.6 µg/l
methylethylketone	0.029	0.004 mg/l	7.10^{-4} mg/l	<0.1 µg/l	<0.1 µg/l

Table 3.1.b - Calculated concentrations of permeated organic matter in the drinking water after 8 hr and 2 days of standing of the drinking water in an HDPE pipe (ϕ = 32 mm, wall thickness 2 mm). The concentrations in the groundwater (C_O) are 10 and 0.1 mg/liter, respectively.

* The permeability coefficients P are determined experimentally.

pipe and an HDPE pipe is slight for the compounds investigated.

3.3 Permeation from soil air

When the drinking water line is located in dry soil, permeation will only take place from the vapor phase. In order to calculate the quantity of organic matter which will permeate through a PE pipe, it is necessary for the concentrations of this compound in soil air to be known.

However, no general techniques are known which permit this concentration to be determined. In many instances, only the total quantity of an organic substance present in the soil is determined (expressed in g per kg dry soil). This is discussed in greater detail in Report No. 86, "Transport of organic compounds through the soil".
Only when the concentration in the vapor phase is known, the quantity of permeated material can be calculated from equation (3.2).

The permeability coefficients for permeation from the vapor phase, P_{vw}, have been determined for a number of compounds using the "flask" method (Table 3.2). As noted in section 3.1, for related compounds the same permeability coefficients can be used as an estimate.

In theory, the permeability coefficient P_{vw} is the same as the permeability coefficient, P_v, which applies for permeation from vapor through a pipe in which air is present in place of drinking water. This means that P_{vw} can be calculated from P_w according to:

$$P_{vw} = \frac{P_w \cdot C_w^{max}}{C_v^{max}} \qquad\qquad (3.4)$$

where: P_{vw} = permeability coefficient "vapor-PE-water" (m^2/day);

P_w = permeability coefficient "water-PE-water" (m^2/day);

C_w^{max} = maximal solubility in water (g/liter);

C_v^{max} = maximal concentration in the vapor phase (g/liter).

In Appendix I, the values of C_w^{max} and C_v^{max} are given for a large number of compounds.

Tables 3.2.a and 3.2.b present, for given concentrations in soil air, the calculated concentrations of permeated material in the drinking water after 8 hr and 2 days of standing of the drinking water in an LDPE and HDPE pipe.

LDPE

Organic compound	$P_{VW}*.10^6$ (m²/day)	C_O = 10 mg/liter		C_O = 0,1 mg/liter	
		t = 2 (day)	t = 0.333 (day)	t = 2 (day)	t = 0.333 (day)
toluene	7.6	6.9 mg/l	1.1 mg/l	69 µg/l	11 µg/l
m-xylene	9.1	8.3 mg/l	1.3 mg/l	83 µg/l	13 µg/l
ethylbenzene	8.3	7.5 mg/l	1.2 mg/l	75 µg/l	12 µg/l
trichloroethylene	8.2	7.4 mg/l	1.2 mg/l	74 µg/l	12 µg/l
tetrachloroethylene	3.5	3.2 mg/l	0.5 mg/l	32 µg/l	5.3 µg/l
chlorobenzene	14.0	12.8 mg/l	2.1 mg/l	128 µg/l	21 µg/l
hexane	0.07	0.06 mg/l	0.01 mg/l	0.6 µg/l	<0.1 µg/l
nonane	0.06	0.06 mg/l	0.01 mg/l	0.6 µg/l	<0.1 µg/l

Table 3.2.a - Calculated concentrations of permeated organic matter in the drinking water after 8 hr and 2 days of standing of the drinking water in an LDPE pipe (ϕ = 32 mm, wall thickness 3.5 mm). The concentrations in soil air (C_O) amount to 10 and 0.1 mg/liter, respectively.

HDPE

Organic compound	$P_{VW}*.10^6$ (m²/day)	C_O = 10 mg/liter		C_O = 0,1 mg/liter	
		t = 2 (day)	t = 0.333 (day)	t = 2 (day)	t = 0.333 (day)
toluene	2.2	3.1 mg/l	0.5 mg/l	31 µg/l	5.2 µg/l
trichloroethylene	4.6	6.5 mg/l	1.1 mg/l	65 µg/l	11 µg/l
tetrachloroethylene	2.2	3.1 mg/l	0.5 mg/l	31 µg/l	5.2 µg/l
chlorobenzene	5.7	8.1 mg/l	1.3 mg/l	81 µg/l	13 µg/l
hexane	0.04	0.06 mg/l	0.009 mg/l	0.6 µg/l	<0.1 µg/l
nonane	0.04	0.06 mg/l	0.009 mg/l	0.6 µg/l	<0.1 µg/l

Table 3.2.b - Calculated concentrations of permeated organic matter in the drinking water after 8 hr and 2 days of standing of the drinking water in an HDPE pipe (ϕ = 32 mm, wall thickness 2 mm). The concentrations in soil air (C_O) are 10 and 0.1 mg/liter, respectively.

* The permeability coefficients P_{VW} are determined experimentally.

4   <u>PVC</u>

The permeation of organic compounds through PVC, if
the concentration of a compound outside of the pipe
is less than 0.1 times the maximal concentration in
water or in the vapor phase, can be described for
all compounds by the two diffusion laws of Fick
(see section 3: polyethylene).

However, the diffusion coefficient is so small that
the time that elapses between the first contact of
the PVC pipe with a contaminant and the achievement
of the steady state (i.e., the situation in which
the flow of material through the pipe wall is con-
stant) will amount to thousands of years. In prac-
tice, therefore, permeation through PVC pipes as a
results of Fickian diffusion will be negligible.

Certain organic compounds, when they are present in
concentrations immediately below the saturation
concentration (> 0.8 times the maximal concentra-
tion), can soften PVC. This gives rise to another
mechanism for the permeation, the so-called "mo-
ving-front". In this situation, significant permea-
tion can take place within a few weeks to months.

In the intermediate range (between 0.1 and 0.8
times the maximal concentration), the permeation
mechanism cannot be simply described. However, the
possibility of permeation occurring cannot be ex-
cluded in this range.

The preceding description is applicable for organic
compounds which can greatly soften PVC, such as
chlorinated hydrocarbons, some anilines, ketones
and nitrobenzenes.

For organic compounds which soften PVC to a lesser extent, such as benzene and alkylated benzenes, no deviation from Fickian diffusion behavior takes place and thus no significant permeation occurs at concentrations up to about 0.25 times the maximal concentration.

For compounds which do not soften PVC at all, no significant permeation can be expected to occur. This is true for compounds such as alcohols, aliphatic hydrocarbons and organic acids.

In summary, this means that no significant permeation occurs for:
- alcohols, aliphatic hydrocarbons and organic acids;
- benzene and alkylated benzenes if the concentration is less than about 0.25 times the maximal concentration;
- chlorinated hydrocarbons, anilines, ketones and nitrobenzenes if the concentration is less than about 0.1 times the maximal concentration.

The maximal concentrations in water and in the vapor phase are presented for various organic compounds in Appendix I.

5   RUBBER RINGS

5.1   Introduction

Rubber rings have a relatively small contact sur-
face with the drinking water. These rings are en-
closed in a coupling which joins piping pieces 2-20
m in length. This means that the permeation through
a rubber ring must be relatively large in order for
it to have a measurable effect on the drinking
water quality.

5.2   Permeation through rubber rings

It is apparent from the results of a model calcula-
tion which is based on realistic assumptions that
the permeation through rubber rings cannot always
be neglected a priori. At high concentrations of
organic compounds in a soil in which pipes are used
containing couplings employing rubber rings, cau-
tion is advisable for the time being. However,
accurate predictions regarding the amount of orga-
nic matter which will permeate through rubber rings
cannot be made at present. More detailed investiga-
tions will be conducted for this purpose with
various types of rubber in combination with various
organic compounds.

6   SELECTION OF METHODS FOR PERMEATION STUDY ON PLAS-
     TIC PIPING MATERIALS

During the investigation on the permeation through
plastic pipes, use was made of various experimental
methods.

I: The "flask" method; here, plastic pipes filled
with drinking water are exposed to a quantity of
the organic compound to be investigated, in water
or in the vapor phase.
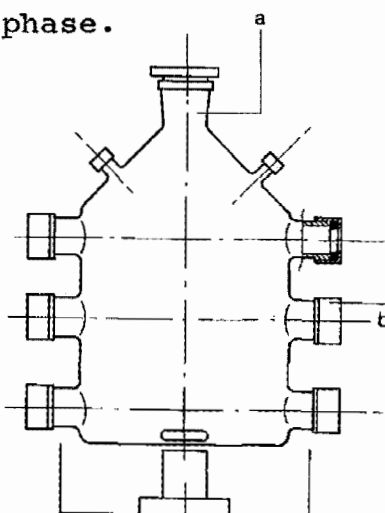
Fig. 6.1 - Equipment for permeation experiments on
             plastic pipes

The experimental equipment consists (see Fig. 6.1)
of a glass bottle (a) with a volume of 10 liter,
provided with screw/clamp connections (b) which
have been mounted in such a way that 3 pieces of
pipe with a diameter of 32 mm may be passed through
this bottle. After mounting the pieces of pipe, the
bottle is filled with the quantity of organic che-
mical to be investigated. The pipes are closed and
are filled with drinking water. The water in the
pipes is examined at regular intervals by gaschro-
matography for the amount of the organic chemical,
in order to calculate the total amount of the pene-

trated chemical Q_t (see Fig. 2.1). The water in the
pipes is renewed after every analysis in order to
keep the concentration in the water in the pipe low
with respect to the outer concentration.

II: The microbalance method; here, with the aid of
a very sensitive balance, the time-dependent ab-
sorption behavior is determined of organic com-
pounds in very thin films cut from a pipe or, in
very small globules of the plastic. The permeabili-
ty coefficient can be calculated from the speed of
weight gain and the final relative weight increase.

III: Liquid immersion; here, pieces of piping are
exposed to the pure organic compound and the maxi-
mum weight increase is determined following esta-
blishment of equilibrium.

According to current insights, the following con-
clusions can be drawn from the investigation with
respect to the methodology.

By design, the "flask" method is in closest agree-
ment with the practical situation.

For investigations regarding the permeation of or-
ganic compounds through polyethylene (or other
rubber polymers), the microbalance method can be
preferred. For the compounds investigated this
method yields results which are in good agreement
with the results of the "flask" method. The time
required for an experiment with the microbalance,
however, is thousands of times shorter than the
time required for an experiment with the "flask"
method. However, the microbalance method is only

applicable for organic compounds with a vapor
pressure in excess of about 1 mbar. For compounds
with a vapor pressure below 1 mbar, the "flask"
method is preferable.
The applicability of liquid immersion is limited to
the preparation of a first global estimate of the
permeation.

The "flask" method is not generally applicable for
investigating permeation through PVC pipes, since
the time that elapses between the first contact of
the pipe with an organic compound and the occurren-
ce of permeation can vary from a few weeks to thou-
sands of years.

Using the microbalance method, it is possible to
very rapidly (within a few days) gain insights into
the permeation behavior of volatile organic com-
pounds (vapor pressure greater than 1 mbar).

For nonvolatile liquid organic compounds via liquid
immersion in a limited time (1-10 months) insight
can be obtained into the permeation behavior.

7   CONCRETE

7.1   Experimental investigation

As described in section 2, the study on the permeability of concrete was performed in a completely empirical fashion. Here, piping pieces 500 mm in diameter and 1 m long are investigated under various extreme conditions. The piping pieces are closed and filled with water wherein a mixture of various organic compounds is dissolved at high but unsaturated concentrations. A pressure of 5 bar is applied to the pipes (internally). Then, the amount of organic contaminant penetrating through the pipe wall is measured on the outside. This situation is very extreme. A (very slight) water flow takes place through the pores in the piping wall. The organic impurities are partly transported to the outside along with the water flow.

Under practical circumstances (pressure on the inside, contaminants on the outside), however, the impurities may diffuse in against the water flow.

In addition, the concrete wall becomes increasingly compact over time under the influence of the water.

7.2   Permeation through concrete

In the above described experiment, it was found that even under these very extreme conditions, almost no permeation takes place through concrete. (Maximally a few µg/liter of water at an average standing time of 40 days.)

Concrete pipes are only available in large diameters (500 mm or more). As a result, drinking water should practically never stagnate in these pipes.

The statement made in the preceding indicates that permeation through concrete will not lead to noticeable effects on drinking water quality in practice.

8   ASBESTOS-CEMENT

8.1   Experimental investigation

The investigation on the permeability of asbestos-
cement pipes is performed with pipelines 100 mm in
diameter. These pipelines are placed in a set-up in
which it is possible to apply pressure both inside
and outside of the pipes. A mixture of organic
impurities in water is applied to the outside of
the pipe.

Three situations were investigated:
1. pressure on the outside (5.5 bar), no pressure
   applied on the inside;
2. no pressure applied on both sides;
3. pressure on the inside (3.5 bar), no pressure
   applied on the outside.

8.2   Permeation through asbestos-cement

It was found in the experiments that several weeks
after the beginning of an experiment, the quantity
of substance which has permeated is small in all
cases (maximally a few µg/liter after an average of
20 days standing at external concentrations of a
few tenths of mg/liter).

Like concrete, asbestos-cement develops a denser
structure over the course of time.
On the basis of the experimental results and in
view of the properties of the material, it can be
concluded that permeation through asbestos-cement
in practice will not lead to noticeable effects on
the drinking water quality.

9   CONCLUSIONS OF THE INVESTIGATION

The results of the laboratory investigation regarding the permeation of organic compounds through various types of drinking water piping materials can be summarized as follows.

9.1   Polyethylene

The permeation through PE water pipes is:
- practically equal for LDPE and HDPE pipes of the same pressure class;
- quite large for lipophilic organic compounds such as alkylated aromatics and chlorinated hydrocarbons. For a PE service line with an external diameter of 32 mm, the concentration of material which has permeated into the drinking water after a standing time of 8 hr is generally more than 1 % of the concentration in the water or vapor phase outside of the pipe;
- low for polar organic compounds such as ketones and phenols. If a PE service line with an external diameter of 32 mm is laid in groundwater contaminated with phenol, for example, the concentration in the drinking water after standing for 8 hr will be less than 0.01 % of the external concentration.

9.2   PVC

No permeation through PVC water pipes will be found for:
- alcohols, aliphatic hydrocarbons and organic acids;
- an individual compound from the group of benzene and alkylated benzenes if the concentration in

groundwater is less than about 0.25 times the maximal solubility in water or if the concentration in soil air is less than about 0.25 times the maximal vapor concentration;

- an individual compound from the groups of anilines, chlorinated hydrocarbons, ketones and nitrobenzenes if the concentration in groundwater is less than about 0.1 times the maximal solubility in water or if the concentration in soil air is less than about 0.1 times the maximal vapor concentration.

9.3 Rubber rings

Significant permeation through rubber rings cannot yet be completely excluded for high concentrations of organic compounds in combination with (very) long stagnation times of the drinking water. The investigation regarding the degree of permeation through rubber rings will be continued by KIWA.

9.4 Concrete and asbestos-cement

Permeation through concrete and asbestos-cement under practical circumstances does not have any noticeable effect on the quality of the drinking water.

10   TRANSPORT OF ORGANIC COMPOUNDS THROUGH THE SOIL

10.1   Introduction

The following section (10.2) shows how a first evaluation can be made of a practical situation. Next, in section 10.3, a mini-scenario is given. This points out the factors to which attention must be paid in order to gain an estimate of the risk. It is noted here that only the technical aspect is considered. The legal and financial aspects were left out of the considerations.

10.2   Evaluation of practical situations

In this section, a presentation is made of the manner in which a first estimate can be made of a practical situation.
For an initial evaluation of the situation, four aspects should be considered sequentially with regard to the contaminating organic compound:
1. the solubility;
2. the mobility;
3. the biodegradation;
4. the volatility.

1. The solubility of organic compounds can vary greatly; this is true for both aliphatic and aromatic compounds (see Table 10.1).

Aliphatics		Aromatics	
Dichloromethane	20.000	Phenol	82.000
1,2-dichloro-ethane	8.700	Benzene	1.780
		Chlorobenzene	500
1,1-dichloro-ethylene	400	1,4-dichloro-benzene	49
Octane	0.66	Diphenyl	7.5

Table 10.1 - Solubilities (mg/liter) in water of a number of organic contaminants

2. The mobility of a substance is determined by the adsorption characteristics of the substance. The adsorption of organic compounds primarily takes place on the organic matter in the soil. The distribution of an organic compound over the liquid phase of the soil and the soil organic matter can be described with the aid of the octanol-water partition coefficient, K_{ow}.

For a practical situation, Karickhoff gave the following equation describing the sorption, expressed by the K_p value:

$$\log K_p = 0.989 \log K_{ow} + \log f_{oc} - 0.21 \qquad (10.1)$$

where: K_p = partition coefficient of the substance over the solid and the liquid phase (cm^3/g)

K_{ow} = partition coefficient of the substance over octanol and water

f_{oc} = fraction of organic matter in the soil.

If the adsorption is known, expressed in K_p, the mobility of the substance with respect to water

he speed at \
peed at which

cs: Chloroethy

compounds:

. 10.1 - Th

mc

th

Sa

Cl

his applies

issolved i

ration. Li

an move ver

can be calculated by means of the equation:

$$\frac{V_{subst.}}{V_{water}} = (1 + \frac{D(1-E)}{E} * K_p)^{-1} = \frac{1}{1 + R_D} \qquad (10.2)$$

with: D   = density of the solid phase

E   = porosity

$V_{subst.}$ = travel rate of the substance in the soil

V_{water} = travel rate of water in the soil

R_D = retardation factor

Fig. 10.1 shows the relative rate of movement of a substance in the soil as a function of the K_{ow}-number.

3. With respect to biodegradation, it is known that the redox potential (a measure of the aerobicity) and the concentration of the substance in question are of great significance for the percent conversion. The redox environment in the unsaturated zone (the region where the soil is not saturated with water) is generally aerobic; the saturated zone can be anaerobic. When the conditions become anaerobic, denitrification begins. When the environment becomes more highly anaerobic, first a sulfate reducing medium develops and subsequently a methane forming medium (see Table 10.2).

The temperature and the pH are also of importance for the biodegradation, although to a lesser degree.
In Table 10.2, the estimated half-lives for the biodegradation are shown insofar as possible; these values were obtained from the literature.

Table 10.2 - Estimated half-lives for biodegradation, derived from the results of the literature

Substance name	Concentration	Aerobic	Redox potential NO_3^--red.	Redox potential CH_4-forming
tetrachloromethane	± 100 µg/l		-21_{25}*	-120_{22}*
	± 10 mg/l	-7_{25}		
trichloromethane	± 100 µg/l	$+175_{20}$	$+56_{25}$*	-112_{35}*
	± 10 mg/l	-21_{25}		
dichloromethane	± 100 µg/l			
	± 10 mg/l	-4_{20}		
chloromethane				
tetrachloroethylene	± 100 µg/l	$+175_{25}$		-56_{35}*
	± 10 mg/l	-21_{25}		
trichloroethylene	± 100 µg/l	$+175_{20}$		120_{35}*
	± 10 mg/l	-14_{25}		
1,1-dichloroethylene	± 10 mg/l	-14_{25}		
chloroethylene				
1,1,1-trichloroethane	± 100 µg/l		-56_{25}*	-54_{35}*
	± 10 mg/l	-28_{25}		
1,2-dichloroethane	± 100 µg/l			175_{35}*
	± 10 mg/l	28_{25}		
2-butanone	± 100 µg/l			
	± 10 mg/l	$+5_{20}$		
pentane				
octane				
benzene	± 10 mg/l	7_{25}		
phenol	± 100 µg/l			$+40_{23}$(?)
	± 10 mg/l	-5_{20}		-56
nitrobenzene	± 100 µg/l	-45_{20}		
	± 10 mg/l	-45_{20}		
chlorobenzene	± 100 µg/l	$+45_{20}$		$+56_{35}$*
	± 10 mg/l	-7_{25}		
1,4-dichlorobenzene	± 100 µg/l	45_{20}		
	± 10 mg/l			
toluene	± 100 µg/l			
	± 10 mg/l	5_{20}		
ethylbenzene	± 100 µg/l	-150*		
propylbenzene				
m-xylene	± 10 mg/l	-3_{20}		
m-di-ethylbenzene				
p-chlorotoluene				
2,4-dichlorotoluene				
diphenyl	± 10 µg/l			
diphenylether				
naphthalene				

* = substrate added.

Remarks: -21_{25}*: indicates that within 21 days, more than half of the compound originally present has been transformed at 25 °C.

$+175_{35}$: indicates that after 175 days, half of the quantity of substance originally present has not yet been converted at 35 °C.

The pH was kept neutral in most tests.

It is apparent from this table that low concentrations of chlorinated alkanes or alkenes, for example, trichloromethane (chloroform), tetrachloroethylene (per) and trichloroethylene (tri) are scarcely broken down at all. Under methane-forming conditions and at elevated temperatures, slow breakdown of these compounds does take place. The benzene compounds are generally degraded under aerobic conditions. Some of them are degraded rapidly, for example, chlorobenzene and m-xylene; others slowly, for example, ethylbenzene.

A number of benzene compounds are known which break down under anaerobic conditions, such as phenol, benzoic acid and phthalic acid.

However, information on biodegradation is not available for many compounds.

4. Finally, the <u>volatility</u> is difficult or impossible to estimate.

10.2.1   Some examples for illustration

A number of properties are presented for some aliphatic and aromatic compounds in Table 10.3a. Table 10.3b presents the speed of movement of these substances relative to the speed of water.

	$C_w$max (mg/l)	$C_v$max (mg/l)	K_{gl}	$\log K_{ow}$ f_{oc}=0.2 %	K_p 1 %	5 %
Aliphatics:						
dichloromethane	20.000	1599	0.079	1.47 0.04	0.18	0.88
trichloroethylene	1100	410	0.37	1.53 0.04	0.20	1.00
tetrachloroethylene	150	124	0.83	2.28 0.22	1.11	5.54
octane	0.66	62	94	4.52 36.4	182.1	910.5
Aromatics:						
phenol	82.000	1.03	$1.25 \cdot 10^{-5}$	1.53 0.04	0.20	1.00
benzene	1700	326	0.19	2.02 0.12	0.61	3.07
chlorobenzene	500	55.7	0.11	2.76 0.66	3.31	16.54
1,4-dichlorobenzene	49	4.8	0.098	3.51 3.65	18.3	91.3
diphenyl	7.5	–	–	3.99 10.9	54.5	272.3

Table 10.3a - Some properties of aliphatic and aromatic compounds, of importance for transport behavior in soil

where: $C_w$max = saturation concentration in water (mg/liter)
$C_v$max = saturation concentration in air (mg/liter)
K_{gl} = partition coefficient over gas and water
K_{ow} = partition coefficient over octanol and water
K_p = partition coefficient over solid and liquid phase in the soil
f_{oc} = percent organic matter in the soil

		$\dfrac{V_{substance}}{V_{water}}$					
foc(%)		0,2		1		5	
E(%)	30	60	30	60	30	60
Aliphatics:							
dichloromethane	0.80	0.94	0.48	0.76	0.16	0.40
trichloroethylene	0.80	0.94	0.45	0.74	0.14	0.37
tetrachloroethylene	0.43	0.72	0.13	0.34	0.03	0.09
octane	$4.5 \cdot 10^{-3}$	0.02	$9.0 \cdot 10^{-4}$	$3.2 \cdot 10^{-3}$	$1.8 \cdot 10^{-4}$	$6.3 \cdot 10^{-4}$
Aromatics:							
phenol	0.80	0.94	0.45	0.74	0.14	0.37
benzene	0.58	0.83	0.21	0.49	0.05	0.16
chlorobenzene	0.20	0.47	0.05	0.15	$2.8 \cdot 10^{-3}$	$9.9 \cdot 10^{-3}$
1,4-dichlorobenzene	0.04	0.14	$6.5 \cdot 10^{-3}$	0.02	$1.8 \cdot 10^{-3}$	$6.3 \cdot 10^{-3}$
diphenyl	0.02	0.05	$3.0 \cdot 10^{-3}$	0.01	$6.1 \cdot 10^{-4}$	$2.1 \cdot 10^{-3}$

Table 10.3b - Speed at which a substance moves in the soil relative to the speed at which water moves for situations with different organic matter contents and different porosities

where: $\dfrac{V_{subst.}}{V_{water}}$ = relative speed of a substance with respect to water
f_{oc} = fraction of organic matter in the soil
E = porosity of the soil

Some of the compounds listed in Tables 10.3a and 10.3b, will be discussed in greater detail. First; trichloroethylene will be considered.

In Table 10.4a, for a number of different types of soil, the distribution of trichloroethylene over the solid, liquid and gaseous phases is presented. This distribution is valid as long as the saturation concentrations of trichloroethylene in water and soil air have not yet been reached.
Table 10.3a shows that the saturation concentrations of tri in water and air are high. It is apparent from the distribution over the phases (Table 10.4a) that relatively large amounts of tri are present in the soil solution. Thus, tri is mobile.

E_g %	E_w %	oc %	conc. solid phase (mg/kg)	conc. water phase (mg/l)	conc. soil air (mg/l)
20	20	1	1	5.00	1.85
5	35	1	1	5.00	1.85
35	5	1	1	5.00	1.85
20	20	0.2	1	25.00	9.25
20	20	5	1	1.00	0.37

Table 10.4a - Distribution of trichloroethylene over solid, liquid and gaseous phases in the case of various gas- and water-filled pore volumes E_g and E_w and various organic matter contents (oc)

It is also evident from Table 10.4a that tri may be present in soil air in non-negligible concentrations. This is of importance since permeation can, likewise, take place from the vapor phase. In addition, a high concentration in soil air also entails the possibility that evaporation may be quite considerable.

With regard to biodegradation, it is apparent from the literature (see Table 10.2) that trichloroethylene is not broken down at low concentrations ($\pm$ 100 µg/liter) under aerobic conditions but will be broken down under highly reducing (methane-forming) conditions.
Higher concentrations of trichloroethylene ($\pm$ 10 mg/liter) are converted to lower concentrations under aerobic conditions.

Secondly; octane will be discussed.

In Table 10.4b, the distribution of octane over the three soil phases is indicated. At a low organic matter content a non-negligible portion of octane is present in soil air.
However, octane has a low saturation concentration in (soil) air, which means that octane is principally distributed over the solid and liquid phases. On the basis of the distribution over solid and liquid phases, it can be concluded that octane principally occurs in the solid phase.

Therefore, octane should display little mobility in the soil.

E_g %	E_w %	oc %	conc. solid phase (mg/kg)	conc. water phase (mg/l)	conc. soil air (mg/l)
20	20	1	1	$5.5.10^{-3}$	0.061
5	35	1	1	$5.5.10^{-3}$	0.061 ·
35	5	1	1	$5.5.10^{-3}$	0.061
20	20	0.2	1	$27.5.10^{-3}$	0.305
20	20	5	1	11.10^{-3}	0.012

Table 10.4b - Distribution of octane over solid, liquid and gaseous phases

Next; benzene is considered:

Benzene has high saturation concentrations in water and soil air (see Table 10.3a).
According to Table 10.4c, a large portion of benzene occurs in the soil solution. Benzene is thus mobile in the aqueous phase.

E_g %	E_w %	oc %	conc. solid phase (mg/kg)	conc. water phase (mg/l)	conc. soil air (mg/l)
20	20	1	1	1.64	0.23
5	35	1	1	1.64	0.23
35	5	1	1	1.64	0.23
20	20	0.2	1	8.33	1.17
20	20	5	1	0.33	0.05

Table 10.4c - Distribution of benzene over the three soil phases

In addition, a non-negligible fraction of benzene occurs in the soil air, so that pipelines can come into contact with benzene via the soil air. Since the benzene concentration in soil air can be high, it is possible for a great deal of benzene to disappear from the soil by evaporation.

Finally; phenol will be discussed:

In Table 10.4d, the distribution of phenol over the three soil phases is presented. Phenol has a very high solubility and a fairly low saturation concen-

E_g %	E_w %	oc %	conc. solid phase (mg/kg)	conc. water phase (mg/l)	conc. soil air (mg/l)
20	20	1	1	5.00	$6.25.10^{-5}$
5	35	1	1	5.00	$6.25.10^{-5}$
35	5	1	1	5.00	$6.25.10^{-5}$
20	20	0.2	1	25.00	$31.25.10^{-5}$
20	20	5	1	1.00	$1.25.10^{-5}$

Table 10.4d - Distribution of phenol over the three soil phases

tration in (soil) air. Therefore, most of the phenol will be present in the soil solution. This means that phenol is mobile. Regarding the biodegradation, it appears that high concentrations of phenol can be broken down both aerobically and anaerobically to low concentrations of phenol. It is not yet clear whether low concentrations of phenol can be broken down.

10.3   A mini-scenario for suspicious situations

In this section, an attempt is made, using a mini-scenario, to indicate the procedures to be followed in suspicious situations. If a "suspicious situation" is involved, a distinction can be made regarding the possible actions to be undertaken in different phases.

Phase 1: Alarm

This is the phase in which it becomes clear that a (permeation) problem is present or may be present. The cause for the alarm must be pursued here: whether it is a finding, a measurement, a health effect or an accident. What is known, what is measured and what is suspected. If the situation so indicates, acute measures have to be taken.

The initiation of further studies in order to gain a good picture of the situation takes a great deal of time. If the concentrations are measured in standing tap water, one has a good idea of whether or not the situation requires acute measures. Acute measures may include direct removal of the source insofar as possible (leaking containers, small amounts of highly contaminated soil, etc.), replacement of the water line by an other type of pipe material or the pumping away of contaminated ground water.

If the substance involved is known, first evaluations can rapidly be made regarding the behavior of the substance in question in the soil (see section 10.2).

Phase 2: Investigation:

If soil contamination takes place in relation to

drinking water, a soil study should be able to provide an answer to the following questions:

1. Which substance(s) is (are) involved?

   What are the characteristics of the substances with regard to:

   - solubility;

   - sorption, depending on the K_{ow} and the organic matter content;

   - volatility;

   - biodegradation.

2. What is the geohydrologic situation at the contamination site?

   - on the soil (for example, disposal site);

   - in the soil;

   - floating on the ground water;

   - dissolved in the ground water;

   - in the surface water;

   - in or near water catchment areas;

   - municipal or rural area;

   - depth of ground water level;

   - type of soil: clay,

                    peat,

                    sand;

   - impermeable clay layer present; at what depth?

   - what is the positioning of the pipes, trench filling?

3. What is the relationship to the water transport pipe?

3a. - main or distribution line: - asbestos-cement

                                 - concrete

                                 - plastic

                                 - cast iron or
                                   steel

3b. - service line: - PVC

                    - PE

                    - steel or copper.

Following the investigation phase, a complete picture of the situation should be available in order to evaluate whether or not the situation is hazardous; if the situation is hazardous, it should be possible to evaluate the (reducing) effect of measures to be taken on the risk.

If a serious risk of soil contamination is under discussion, consideration may be given to taking measures based on the Interim Law on Soil Clean-up (make contact with the provincial and/or regional inspectorate for the environment).

Table 10.5 shows the concentration levels beginning from which a situation may fall under this law and when more detailed studies or clean-up tests need to be made. This table forms only a portion of the testing scope (see Soil Clean-up Guidlines).

Once this evaluation has been performed, temporary measures can be taken while awaiting further clean-up if necessary.

Phase 3: Clean-up:
Phase in which measures are taken. This phase is not performed if the investigation phase indicates that the situation is not dangerous.

Possible clean-up measures may include: replacement of drinking water lines, digging of protective wells, introduction of plastic sheaths or the like around the contamination source, combined with pumping in order to prevent spread of contaminated ground water, or removal of the soil contamination source.

Table 10.5 - Testing table maintained in the Interim Law on Soil Clean-up for evaluating the concentration levels of various contaminations in the soil*.

Occurrence in:	Soil (mg/kg dry soil)			Ground water (µg/l)		
Level:	A**	B	C	A**	B	C
Component:						
benzene	0.01	0.5	5	0.2	1	5
ethylbenzene	0.05	5	50	0.5	20	60
toluene	0.05	3	30	0.5	15	50
xylenes	0.05	5	50	0.5	20	60
phenols	0.02	1	10	0.5	15	50
aromatics (total)	0.1	7	70	1	30	100
naphthalene	0.1	5	50	0.2	7	30
aliphatic chloro- (individual)	0.1	5	50	1	10	50
aliphatic chloro- (total)	0.1	7	70	1	15	70
chlorobenzenes (individual)	0.05	1	10	0.02	0.5	2
chlorobenzenes (total)	0.05	2	20	0.02	1	5
EOX (total)	0.1	8	80	1	15	70
gasoline	20	100	800	10	40	150
mineral oil	100	1000	5000	20	200	600

* The concentration should be considered in combination with the use of the soil and local contamination situation.

** A: Reference value

B: Level B is the test value above which further investigation is desirable

C: Level C is the test value above which clean-up investigations are necessary

From: Soil Clean-up Guidelines, VROM, 1983

11   <u>RESPONSIBILITY</u>

The research project "Effects of Soil Contamina-
tions and Piping Materials on Drinking Water Quali-
ty" was financed in equal parts by the Netherlands
Waterworks Association (VEWIN), the Department of
Housing, Physical Planning and Environment (VROM)
and the Manufacturers of Drinking Water Pipes made
of Plastic, Asbestos-cement and Concrete.

The investigation was monitored by the Technical
Coordinating Group on Permeation and the Steering
Group on Permeation. The Technical Coordinating
Group agreed to perform the direct monitoring of
this study; the Steering Group was responsible for
monitoring the administrative aspects and general
progress.

The makeup of these groups is as follows.

Technical Coordinating Group on Permeation
- Ir. J. Schilperoord (KIWA N.V.), chairman;
- Ir. J. de Feijter (KIWA N.V.), secretary;
- Ir. J.W. Aeyelts Averink (Shell International
  Research Co.);
- Ir. C.G.E.M. van Beek (KIWA N.V.);
- Dr. P. Benjamin (Draka-Polva B.V.);
- Ir. W.F. Geene (Bonna-Vianen);
- Ir. H.J. van 't Haaff (Eternit B.V.);
- Drs. B.G. van der Heijden (Rotterdam Waterworks);
- Drs. W. van de Meent (KIWA N.V.);
- Ir. J.B.H.J. Linders (National Institute of
  Public Health and Environmental Hygiene);
- Prof. Dr. A.J. Staverman (State University of
  Leiden);

- Dr. T. Trouwborst (Department of Housing, Physical Planning and Environment);
- Drs. G. Veenendaal (KIWA N.V.);
- Prof. Dr.Ir. A.K. van der Vegt (Delft University of Technology);
- Dr. M.W. Vonk (KIWA N.V.).

Steering Group on Permeation

- Ir. P.J. Verkerk (Directorate Drinking and Industrial Water Supply, Department of Housing, Physical Planning and Environment), chairman (until January 1, 1985);
- Drs. W.E.M.C. Krul (Directorate Drinking and Industrial Water Supply, Department of Housing, Physical Planning and Environment), chairman (from January 1, 1985);
- Drs. G. Veenendaal (KIWA N.V.), secretary;
- Dr. P. Benjamin (Draka-Polva B.V.) in the name of the industrial group;
- Ir. J. Schilperoord (KIWA N.V.), chairman of Technical Coordinating Group on Permeation;
- Ir. A.M. Stofberg (Gelderland Waterworks) in the name of VEWIN;
- Ir. W.C. Wijntjes (Groningen Municipal Waterworks) in the name of VEWIN.

APPENDIX I: PHYSICAL CHEMICAL PROPERTIES OF A NUMBER OF ORGANIC COMPOUNDS

I.1 Introduction

In this Appendix, the maximal solubility (S) in LDPE and HDPE (in grams of organic compound per gram of polymer), the maximal solubility in water (C_w^{max}) and the maximal concentration in the vapor phase at 20 °C (C_v^{max}) are given, the last two in mg/liter.

The organic compounds are divided into groups, namely, aromatics (I-1); alkanes (I-2); alkenes (I-3); chlorinated aromatics (I-4); chlorinated alkanes and alkenes (I-5); ethers, ketones and alcohols (I-6); nitrobenzenes, anilines and chlorophenols (I-7).

I.2 Solubility in LDPE and HDPE

The solubilities S of organic compounds in LDPE and HDPE are determined within the scope of the permeation study using liquid immersion experiments. In this experiment, a piece of pipe is immersed in a pure organic liquid or placed in a closed vessel together with the solid organic compound.

By regularly measuring the weight gain of the piece of piping information is obtained regarding the quantity of organic matter that dissolves in the polymer. When the weight of the piece of piping no longer increases over time, i.e., the equilibrium situation has been reached, the maximum solubility can be determined from the weight gain.

I.3 Solubility in water

The values obtained for the solubility in water have been gathered from the literature. However, the solubility depends among others on:
- temperature
- type of water (with or without salt and the like).

This means that the values reported here should be regarded as reference values.

I.4 Maximal concentration in the vapor phase

The maximal vapor pressure P_o is calculated with the aid of the following equation:

$$^{10}\log P_o = (- 0.2185 \frac{A}{T}) + B$$

where: A = molar heat of vaporization;
B = material constant;
P_o = maximal vapor pressure (in mm Hg);
T = temperature (K).

The values for A and B are obtained from the literature.
The maximal concentration in the vapor phase is calculated from the maximal vapor pressure with the aid of:

$$C_v^{max} = \frac{0.012 \, P_o \cdot M_w}{T}$$

where: C_v^{max} = maximal vapor concentration (g/liter);

P_O = maximal vapor pressure (mbar);

M_w = molecular weight;

T = temperature (K).

Table I-1 - Aromatics

Compound	General formula	S_{LDPE} (g/g)	S_{HDPE} (g/g)	C_w^{max} (mg/liter)	C_v^{max} (mg/liter)
benzene	C_6H_6	0.105	0.070	1780	326
toluene	C_7H_8	0.116	0.076	515	111
styrene	C_8H_8	-	-	300	29
o-xylene	C_8H_{10}	0.121	0.080	175	29
m-xylene	C_8H_{10}	0.118	0.079	190	35
p-xylene	C_8H_{10}	0.124	0.081	198	38
ethylbenzene	C_8H_{10}	0.101	0.068	152	41
1,2,3-trimethylbenzene	C_9H_{12}	-	-	-	8
1,2,4-trimethylbenzene	C_9H_{12}	-	-	-	11
1,3,5-trimethylbenzene	C_9H_{12}	0.115	0.079	20	14
propylbenzene	C_9H_{12}	0.096	0.066	60	17
isopropylbenzene	C_9H_{12}	-	-	50	23
o-ethyltoluene	C_9H_{12}	-	-	-	14
m-ethyltoluene	C_9H_{12}	-	-	-	16
p-ethyltoluene	C_9H_{12}	-	-	-	16
naphthalene	$C_{10}H_8$	-	-	30	0.4
isobutylbenzene	$C_{10}H_{14}$	-	-	17	8.9
p-isopropyltoluene	$C_{10}H_{14}$	-	-	34	-
diphenyl	$C_{12}H_{10}$	-	-	7.5	0.3
diphenylether	$C_{12}H_{10}O$	-	-	21.0	0.5
1,3,5-triethylbenzene	$C_{12}H_{18}$	-	-	7.0	-
anthracene	$C_{14}H_{10}$	-	-	1.3	0.8
phenanthrene	$C_{14}H_{10}$	-	-	1.6	0.4

C_9H_{12}-isomers : P_o varies from about 1.7 to 3.5 mbar

$C_{10}H_{14}$-isomers: P_o varies from about 1.5 to 2.4 mbar

- : data unknown

Table I-2 - Alkanes

Compound	General formula	S_{LDPE} (g/g)	S_{HDPE} (g/g)	C_w^{max} (mg/liter)	C_v^{max} (mg/liter)
methane	CH_4	-	-	24.4	*
ethane	C_2H_6	-	-	60.4	*
propane	C_3H_8	-	-	62.4	*
butane	C_4H_{10}	-	-	61.4	*
2-methylpropane	C_4H_{10}	-	-	49	*
cyclopentane	C_5H_{10}	-	-	156.0	995
pentane	C_5H_{12}	0.080	0.051	38.5	1700
iso-pentane	C_5H_{12}	-	-	47.8	2065
2,2-dimethylpropane	C_5H_{12}	-	-	33.2	*
cyclohexane	C_6H_{12}	0.132	0.079	55.0	356
hexane	C_6H_{14}	0.082	0.053	9.5	566
2-methylpentane	C_6H_{14}	-	-	13.8	785
3-methylpentane	C_6H_{14}	-	-	12.8	703
2,2-dimethylbutane	C_6H_{14}	-	-	18.4	1240
cycloheptane	C_7H_{14}	-	-	30.0	-
heptane	C_7H_{16}	-	-	3.0	192
2,4-dimethylpentane	C_7H_{16}	-	-	4.1	407
cyclo-octane	C_8H_{16}	-	-	7.9	-
octane	C_8H_{18}	0.079	0.053	0.7	69
2,2,4-trimethylpentane	C_8H_{18}	0.065	0.045	2.4	-
2,3-dimethylhexane	C_8H_{18}	-	-	0.13	-
nonane	C_9H_{20}	-	-	0.45	24

C_6H_{14}-isomers : P_o varies from about 160 to 350 mbar
C_7H_{16}-isomers : P_o varies from about 43 to 106 mbar
C_8H_{18}-isomers : P_o varies from about 18 to 33 mbar

* : a gas at 20 °C
- : data unknown

Table I-3 - Alkenes

Compound	General formula	S_{LDPE} (g/g)	S_{HDPE} (g/g)	c_w^{max} (mg/liter)	c_v^{max} (mg/liter)
ethyne	C_2H_2	-	-	-	*
ethylene	C_2H_4	-	-	131	*
propylene	C_3H_6	-	-	200	*
1,2-butadiene	C_4H_6	-	-	-	*
1,3-butadiene	C_4H_6	-	-	-	*
butene-1	C_4H_8	-	-	222	-
2-methylpropene	C_4H_8	-	-	263	*
isoprene	C_5H_8	-	-	-	1870
1,3-pentadiene	C_5H_8	-	-	-	1260
1,4-pentadiene	C_5H_8	-	-	-	2400
cyclopentane	C_5H_8	-	-	535	-
pentene-1	C_5H_{10}	-	-	148	-
pentene-2	C_5H_{10}	-	-	203	-
3-methyl-1-butene	C_5H_{10}	-	-	130	-
cyclohexene	C_6H_{10}	-	-	213	-
1-hexene	C_6H_{12}	-	-	50	613
2-methyl-1-pentene	C_6H_{12}	-	-	78	-
4-methyl-1-pentene	C_6H_{12}	-	-	48	-
cycloheptene	C_7H_{12}	-	-	66	-
2-heptene (cis)	C_7H_{14}	-	-	15	190
1-octene	C_8H_{16}	-	-	2.7	-

C_7H_{14}-isomers : P_0 varies from about 39 to 47 mbar

C_8H_{16}-isomers : P_0 varies from about 12 to 22 mbar

* : a gas at 20 °C

- : data unknown

Table I-4 - Chlorinated aromatics

Compound	General formula	S_{LDPE} (g/g)	S_{HDPE} (g/g)	c_w^{max} (mg/liter)	c_v^{max} (mg/liter)
chlorobenzene	C_6H_5Cl	0.136	0.092	500	58
1,2-dichlorobenzene	$C_4H_4Cl_2$	0.137	0.100	100	7.5
1,3-dichlorobenzene	$C_6H_4Cl_2$	0.167	0.115	123	14
1,4-dichlorobenzene	$C_6H_4Cl_2$	0.044	0.035	49	4.8
1,2,3-trichlorobenzene	$C_6H_3Cl_3$	0.042	0.034	12	-
1,2,4-trichlorobenzene	$C_6H_3Cl_3$	0.159	0.117	19	-
1,3,5-trichlorobenzene	$C_6H_3Cl_3$	0.044	0.036	5.8	-
1,2,3,4-tetrachlorobenzene	$C_6H_2Cl_4$	-	-	3.5	-
1,2,3,5-tetrachlorobenzene	$C_6H_2Cl_4$	-	-	2.4	-
1,2,4,5-tetrachlorobenzene	$C_6H_2Cl_4$	-	-	0.3	-
pentachlorobenzene	C_6HCl_5	0.007	0.005	0.24	0.08
hexachlorobenzene	C_6Cl_6	-	-	0.005	$1,2.10^{-4}$
o-chlorotoluene	C_7H_7Cl	0.144	0.097	-	19
m-chlorotoluene	C_7H_7Cl	0.127	0.089	-	19
p-chlorotoluene	C_7H_7Cl	0.128	0.089	-	18
α,α-dichlorotoluene	$C_7H_6Cl_2$	-	-	-	3.3
α,α,α-trichlorotoluene	$C_7H_5Cl_3$	0.104	0.091	-	-
1-chloro-2-ethylbenzene	C_8H_9Cl	-	-	-	10
1-chloro-3-ethylbenzene	C_8H_9Cl	-	-	-	9
1-chloro-4-ethylbenzene	C_8H_9Cl	-	-	-	8
2-chlorobiphenyl	$C_{12}H_9Cl$	-	-	5.8	-
3-chlorobiphenyl	$C_{12}H_9Cl$	-	-	3.3	-
4-chlorobiphenyl	$C_{12}H_9Cl$	-	-	0.8	-
4,4-dichlorobiphenyl	$C_{12}H_8Cl_2$	-	-	0.062	-
DDE	$C_{14}H_8Cl_4$	-	-	0.040	-
DDT	$C_{14}H_9Cl_5$	-	-	0.031	$3,5.10^{-6}$

- : data unknown

Table I-5 - Chlorinated alkanes and alkenes

Compound	General formula	S_{LDPE} (g/g)	S_{HDPE} (g/g)	C_w^{max} (mg/liter)	C_v^{max} (mg/liter)
dichloromethane	CH_2Cl_2	0.105	0.078	20000	1625
trichloromethane	$CHCl_3$	-	-	8000	1050
tetrachloromethane	CCl_4	0.281	0.174	800	760
1,2-dichloroethylene	$C_2H_2Cl_2$	0.195	0.126	800	1035
trichloroethylene	C_2HCl_3	-	-	1100	411
tetrachloroethylene	C_2Cl_4	0.295	0.185	150	125
chloroethane	C_2H_5Cl	-	-	5700	-
1,2-dichloroethane	$C_2H_4Cl_2$	0.058	0.046	8700	334
1,1,1-trichloroethane	$C_2H_3Cl_3$	0.158	0.108	4400	700
1,1,2-trichloroethane	$C_2H_3Cl_3$	-	-	4500	139
1,1,2,2-tetrachloroethane	$C_2H_2Cl_4$	0.105	0.084	2900	46
pentachloroethane	C_2HCl_5	-	-	-	37
hexachloroethane	C_2Cl_6	-	-	-	17
n-chloropropane	C_3H_7Cl	-	-	2300[1]	1190
2-chloropropane	C_3H_7Cl	-	-	3400[1]	1425
1,2-dichloropropane	$C_3H_6Cl_2$	0.075	0.056	2700	246
1,3-dichloropropane	$C_3H_6Cl_2$	-	-	2870[2]	-
1,2,3-trichloropropane	$C_3H_5Cl_3$	-	-	-	17
n-chlorobutane	C_4H_9Cl	-	-	660[1]	410
1,2-dichlorobutane	$C_4H_8Cl_2$	-	-	-	107
1,2,3-trichlorobutane	$C_4H_7Cl_3$	-	-	-	30
lindane (γ)	$C_6H_6Cl_6$	-	-	10	-
aldrin	$C_{12}H_8Cl_6$	-	-	0.01	$4,5.10^{-4}$
dieldrin	$C_{12}H_8Cl_6O$	-	-	0.1	$3,6.10^{-6}$

- : data unknown

[1]: applicable at 12 °C

[2]: applicable at 30 °C

Table I-6 - Ethers, ketones and alcohols

Compound	General formula	S_{LDPE} (g/g)	S_{HDPE} (g/g)	c_w^{max} (mg/liter)	c_v^{max} (mg/liter)
diethylether	$C_4H_{10}O$	-	-	69000	1800
dipropylether	$C_6H_{14}O$	-	-	-	300
diisopropylether	$C_6H_{14}O$	0.055	0.039	9000	712
di-(chloroisopropyl)ether	$C_6H_{12}OCl_2$	-	-	1700	-
dibutylether	$C_6H_{18}O$	-	-	300	35
acetone	C_3H_6O	-	-	∞	520
methylethylketone	C_4H_8O	0.019	0.018	267000	302
2-pentanone	$C_5H_{10}O$	-	-	60000	56
ethylisobutylketone	$C_6H_{12}O$	-	-	17000	33
2-heptanone	$C_7H_{14}O$	-	-	4300	17
methoxybenzene	C_7H_8O	-	-	-	18
ethanol	C_2H_5OH	0.001	0.002	∞	111
1-propanol	C_3H_7CH	-	-	-	47
1-butanol	C_4H_9OH	-	-	77000	18
isobutanol	C_4H_9OH	-	-	95000	41
1-pentanol	$C_5H_{11}OH$	-	-	26000	14
3-methyl-1-butanol	$C_5H_{11}OH$	-	-	27500	-
1-hexanol	$C_6H_{11}OH$	0.004	0.004	5900	5.5
cyclohexanol	$C_6H_{11}OH$	-	-	36000	5.3
2-ethyl-1-hexanol	$C_8H_{17}OH$	-	-	1000	0.4

- : data unknown

Table I-7 - Nitrobenzenes, anilines and chlorophenols

Compound	General formula	S_{LDPE} (g/g)	S_{HDPE} (g/g)	c_w^{max} (mg/liter)	c_v^{max} (mg/liter)
nitrobenzene	$C_6H_5NO_2$	0.018	0.017	1900	1.5
o-dinitrobenzene	$C_6H_4N_2O_4$	-	-	100	-
m-dinitrobenzene	$C_6H_4N_2O_4$	-	-	469	-
p-dinitrobenzene	$C_6H_4N_2O_4$	-	-	-	-
2-chloroaniline	C_6H_6NCl	0.023	0.022	-	< 0.5
3-chloroaniline	C_6H_6NCl	0.011	0.011	-	105
4-chloroaniline	C_6H_6NCl	0.004	0.003	-	0.11
o-nitroaniline	$C_6H_6N_2O_2$	-	-	1260	< 0.6
m-nitroaniline	$C_6H_6N_2O_2$	0.001	0.002	890	-
p-nitroaniline	$C_6H_6N_2O_2$	-	-	800	0.011
aniline	C_6H_7N	0.006	0.005	34000	5.0
o-nitrotoluene	$C_7H_7NO_2$	-	-	652	0.73
m-nitrotoluene	$C_7H_7NO_2$	-	-	498	0.73
p-nitrotoluene	$C_7H_7NO_2$	-	-	442	0.73
n-methylacetanilide	$C_9H_{11}NO$	-	-	-	0.25
ethylcarbanilate	$C_9H_{11}NO_2$	-	-	-	$3.8.10^{-3}$
phenol	C_6H_5OH	0.002	0.001	82000	0.98
p-chlorophenol	C_6H_4OHCl	0.004	0.004	27000	0.69
2,4-dichlorophenol	$C_6H_3OHCl_2$	-	-	4500	-
2,3,5-trichlorophenol	$C_6H_2OHCl_3$	0.007	0.006	-	-
2,4,6-trichlorphenol	$C_6H_2OHCl_3$	0.014	0.012	800	-
2,4,5-trichlorphenol	$C_6H_2OHCl_3$	-	-	1190	-
2,3,5,6-tetrachlorophenol	C_6HOHCl_4	0.003	0.002	-	-
2,3,4,6-tetrachlorophenol	C_6HOHCl_4	-	-	-	-
pentachlorophenol	C_6OHCl_5	0.001	0.001	14	$1.1.10^{-3}$

- : data unknown