Journal of Hydroscience and Hydraulic Engineering
Vol. 8, No. 1, October, 1990, 79-88

INFILTRATION AND LEACHING OF CHLORINATED ORGANIC COMPOUNDS AND MECHANISM OF GROUNDWATER CONTAMINATION

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SYNOPSIS

Organochlorines have been widely detected in the groundwater in Japan. In order to resolve the mechanism of groundwater pollution, migration and leaching of the undiluted organochlorines were examined in water and porous media. It proves that undiluted trichloroethylene(TCE) readily infiltrated in unsaturated zone due to the physical properties, greater in density and less in surface tension and viscosity than water. In saturated zone TCE migrated and remained stagnant as isolated in pore space of the media. These phenomena reappeared in the Hele-Shaw model. Leachate concentration of TCE due to the rainfall infiltration and groundwater flow amounts to several thousands times as much as the standard for drinking water. Besides, a new monitoring method by analysing the gaseous contents in the surface soil has been developed and was applied to the field observation in the waste landfill site.

This paper is a kind of reviews on hydraulic study of groundwater contamination mechanism due to chlorinated organic compounds. This subject seems new since this contamination was well known in the world, and the related researches have been not so many performed. The present review, therefore, is focused on the research results of the authors themselves and some related informations in Japan.

PRESENT STATUS OF GROUNDWATER CONTAMINATION

Groundwater contamination with organochlorines such as trichloroethylene is said to be a new type of environmental pollution because, as substances of great industrial use, organochlorines have been produced and used in huge amounts, often leading to groundwater contamination in cities and towns where their consumption is large, and also because they are reported to cause cancer if orally taken repeatedly for a long period of time even if in slight amounts each time. Statistics in 1986 showed that the production of trichloroethylene (hereafter referred to as TCE), tetrachloroethylene (PCE) and 1,1,1-trichloroethane(TCA) was 71,000 tons, 70,000 tons and 128,000 tons, respectively.

Concerning the degree of groundwater contamination with organochlorines in Japan, an environmental survey made in 1982 by the Japan Environment Agency(6) showed that about one-third of the 1,499 samples collected from different wells contained TCE, with 3% of them having a TCE content above the limits specified in the current WHO (World Health Organization) guideline.

In response to this, the Ministry of Health and Welfare in 1984 set up tentative standards for drinking water: 0.03mg/l or below, 0.01mg/l or below and

0.3mg/l or below for TCE, PCE and TCA, respectively.

Local governments have been conducting groundwater contamination surveys since 1984. Table 1 shows the results of these surveys performed during a three-year period beginning in 1984 and compiled by Environment Agency(Hayakawa(1)). The surveys covered about 12,000 wells. In terms of the average over the three-year period, 3.3%, 3.6% and 0.1% of the samples exceed the drinking water standards, indicating that groundwater is contaminated with organochlorines in almost all parts of the nation.

Table 1 Survey Results on Groundwater Contamination with Organochlorines (1984-1986) (Hayakawa, 1988(1))

	Contaminant	Number of city,town	Number of observed well	Number of well over standards	Ratio of excess (%)
1984	TCE	833	5720	122	2.1
	PCE		5733	185	3.2
	TCA		5476	4	0.1
1985	TCE	468	3461	123	3.6
	PCE		3459	140	4.0
	TCA		3455	8	0.2
1986	TCE	303	2794	146	5.2
	PCE		2777	109	3.9
	TCA		2763	3	0.1
Total	TCE	–	11975	391	3.3
	PCE	–	11969	434	3.6
	TCA	–	11694	15	0.1

note 1)TCE:Trichloroethylene, PEC:Tetrachloroethylene, TCA;1,1,1-trichloroethane.
2)Observed wells are different in each year.
3)Provisional standards as to drinking water are TCE:0.03mg/l, PCE:0.01mg/l and TCA:0.3mg/l (less than).

HISTORY AND ROLE OF RESEARCH

Investigation of Contamination Mechanism

Once contaminated groundwater is detected in an area, a study should be first made to identify the cause of contamination and route of the contaminants getting into groundwater.

Possible causes and routes include the following(Muraoka(10) and Nakasugi(13)):

1) Originating in atmosphere
2) Originating in waste water
3) waste landfill site
4) Accident such as cracking in solvent tank
5) Disposal of waste solvent in well

Rainfall is one of the factors in category 1). However,though rain may contain about 1μg/l organochlorines, such a low concentration would not cause a significant level of groundwater pollution that might come into question. Compared to this, serious groundwater pollution would occur if waste water with a high content of organochlorines continues to leak through joints of concrete channels or other channels excavated without timbering, and infiltrates into the ground over a long period of time.

In addition, distillation residue and filters used for solvent recovery contain almost undiluted solution of these substances. The substances will infiltrate into the ground if waste containing such undiluted solution is used as material for land reclamation or if there are cracks in a solvent tank or damaged joints in piping (Fig.1). Not to mention the accident in Silicon Valley, this will cause serious groundwater pollution.

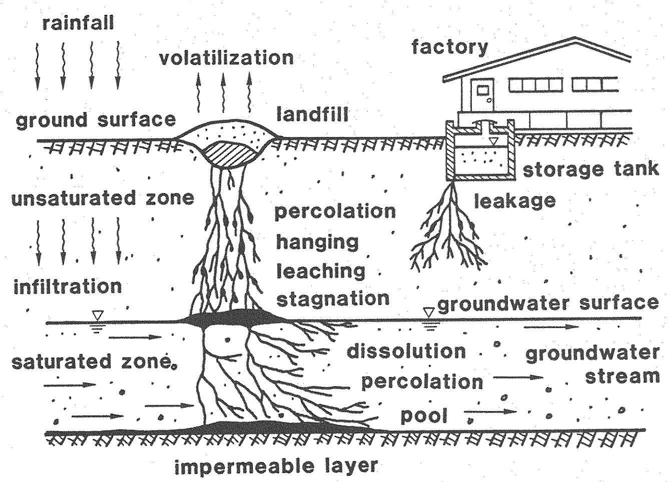


Fig.1 Example of Leakage from Underground Tank or Landfill Site

Organochlorines dissolved in water are mainly affected by the flow of the water and expected to show behaviors similar to those of the water. However, these compounds, including TCE, have the feature of being considerably larger in density while smaller in viscosity and surface tension than water. This suggests that when infiltrating into the ground, undiluted solution of these substances might show unexpected behaviors which cannot be predicted by the conventional hydraulic theories. In view of this, we have made a series of experiments to investigate the infiltration(Muraoka et al.(8) and Jinno(7)) and dissolution(Hirata et al.(2)) of undiluted TCE solution using glass beads and Kanuma soil as model soil.

Groundwater Pollution Monitoring

A study to purify contaminated groundwater should be performed along with analysis of the contamination mechanism. For this, it is essential to obtain data on the contamination source, including information on the route and amount of contaminants entering the environment. However, one could only suggest a possible contamination source in the most successful case while definite identification of a source may be impossible in most cases. There are two major reasons for this. First, little information can be obtained on the flow of groundwater and second, as useful solvents, these substances, including TCE, are produced in huge amounts, several tens of thousands of tons each year, and used for a variety of applications, probably with many user plants in the urban area. The quality of groundwater cannot be determined if there is no well or spring water, and there may not always exist properly arranged wells in the area to be surveyed. With such background, we have also made an effort at the development of a monitoring technique useful for the identification of contamination sources and detailed analysis of the spread of contaminants in groundwater. Organochlorines are volatile and by making use of this feature, a soil/groundwater contamination detection system was developed in which substances in the air contained in the surface soil are used as indications.

The present report addresses experiments for analyzing the groundwater contamination mechanism and describes the present status of monitoring by soil gas.

BEHAVIOR AND DISSOLUTION MECHANISM OF UNDILUTED TCE SOLUTION IN WATER, SOIL AND GROUNDWATER

Experiment with Undiluted TCE Solution Poured in Well

The first of a series of laboratory experiments was designed for the analysis of undiluted TCE solution poured in a well. The experiment used model wells made of Pyrex, 10, 5 and 2.5cm in inside diameter and 3m in depth. Undiluted TCE solution was poured in them. The volume of the solution is corresponding to a 5cm depth of each well (392.7, 98.2 and 24.5ml for the 10, 5 and 2.5cm diameter wells, respectively). Then, the behaviors of the solution falling in the water and its solubility in groundwater were observed(Muraoka et al.(11)).

Organochlorines are higher in density and smaller in viscosity and surface tension than water. Therefore, the solution breaks into drops immediately after being poured, and falls in the form of drops with diameter up to about 15mm. The falling rate of the drops differ with their diameter, causing them to disperse as they fall. It is not easy, however, to explain exactly the characteristics of dispersion and falling resistance of the group of drops, so the topic here will be limited in the solubility of organochlorine in the well water. Fig.2 illustrates the TCE concentration in the well water observed after the falling test. The average concentration is 141, 131 and 119mg/l in the sequence of the well diameter (from large to small). The values are 4,700 to 4,000 times as large as the standard values for drinking water.

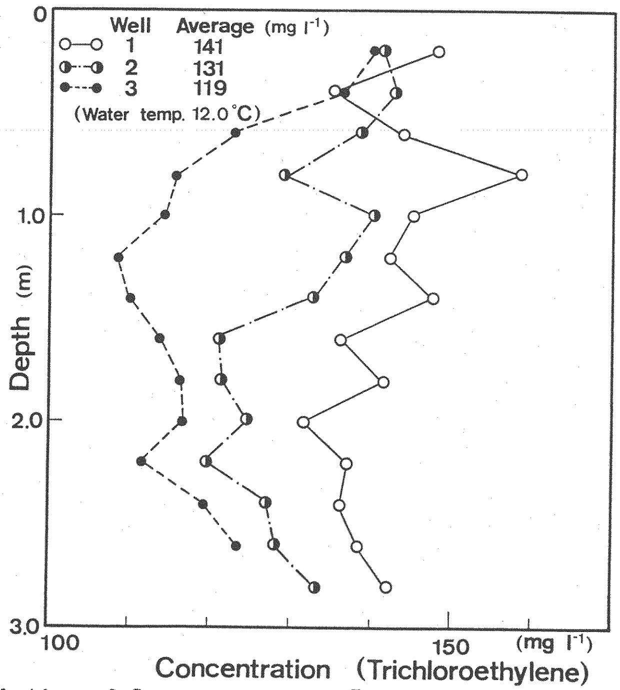


Fig.2 Distribution of Concentration of Trichloroethylene in Model Well. (Diameters: 10cm for Well 1, 5cm for Well 2, 2.5cm for Well 3)

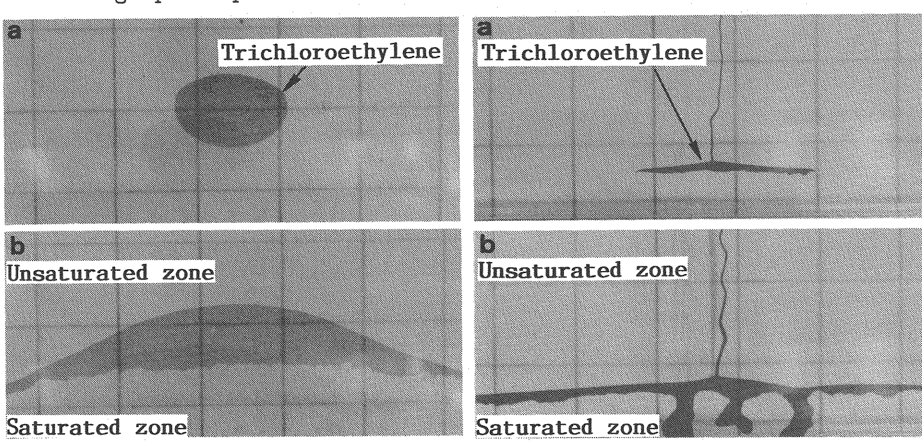
Infiltration in Soil and Groundwater

Test for the infiltration of undiluted TCE solution was carried out using glass beads and Kanuma soil as model soil. A glass column of 6cm in inside diameter and 40cm in depth was filled with model soil, and infiltration tests were made for three cases: 1) unsaturated, 2) saturated, and 3) unsaturated in the upper half and saturated in the lower half(Hirata et al.(3)). Results showed the following: (a) Being smaller in viscosity and surface tension than water, such substances as TCE infiltrate more rapidly than water in unsaturated soil, and if each grain has many pore spaces (aggregation) as in Kanuma soil, they get into these pore spaces, and (b) After TCE reaches the groundwater surface through the unsaturated zone, it gets in the saturated zone and remains stagnant between grains when the soil grains are large in diameter (approximately larger than 3mm) and have equivalent large pores. The undiluted TCE solution stays on the groundwater surface if the grain size is small (approximately smaller than 1mm), but can infiltrate into the pore of saturated zone in case of the test that the groundwater surface moves up and down with 5cm amplitude and three cycles in an hour.

The hele-shaw model is useful to simulate solution in and around the capillary zone existing between the unsaturated and saturated zones. The test for infiltration of undiluted TCE solution was performed using two glass plates (35cm×50cm) with a spacing of 0.1 or 0.2mm between them(Hirata et al.(3)).

Fig.3A illustrates visible test results made with a spacing of 0.1mm. The amount of solution poured from above the glass plates is in the range of 0.2-0.3ml, and the distance between the grid lines in the photograph is 5cm. In this case, TCE, after infiltrating through the unsaturated zone (the void existing above the capillary zone), stayed on the capillary zone. It did not infiltrate into the saturated zone though the TCE added sometimes increased the thickness of the capillary zone. The test with the 0.1mm spacing is considered to correspond to infiltration in porous material with small grain and pore size.

Fig.3B shows test results with a spacing of 0.2mm. Unlike the case in Fig.3A, the TCE poured from above infiltrates into the unsaturated zone in a streak-like manner. Then TCE on the groundwater surface works to form fingers in a portion where the balance between the gravity and capillary force breaks, resulting in infiltration of TCE into the saturated zone. A similar process may occur in porous media with large pore spaces.



A (0.1mm) B (0.2mm)

Fig.3 Infiltration of Trichloroethylene Analyzed with Hele-Shaw Model

Infiltration of Rain and Leaching of TCE by Groundwater Flow

As shown in Fig.1, the actual soil sphere contains vertically infiltrated rainwater, while groundwater is flowing horizontally in the groundwater sphere. A test was also carried out for leaching of TCE infiltrated in soil or groundwater(Hirata et al.(2)), taking the actual groundwater flow into account. For the leaching test with infiltrated rainwater, a cylindrical column of 6cm in diameter and 20cm in depth(shown in Fig.4) was filled with dry Kanuma soil (average grain diameter 1.5mm), and an appropriate amount of undiluted TCE solution was placed in it. Then, pure water, simulating rainwater, is poured onto the Kanuma soil column (rainfall intensity 10mm/hr), and the TCE concentration in the leachate was observed. Results are illustrated in Fig.4. It can be seen that TCE is leached in a concentration of 1,000mg/1, which is close to the solubility at saturation (1,100mg/1 at 25°C). This concentration is 33,000 times as high as the standard value (0.03mg/l) for drinking water.

For the test for leaching by groundwater flow, 2g of undiluted TCE solution is placed in the middle site of a cylindrical column as shown in Fig.4 which contains grass beads (average grain size 3mm) to form a saturated zone. Then, groundwater is passed through the cylindrical column at a rate of 1m/day and the TCE concentration in the leachate is measured. Results (Fig.5) indicate that TCE is leached in a high concentration of 60mg/l, though it is lower than the concentration of TCE leaching by infiltrated rainwater(Hirata et al.(4)).

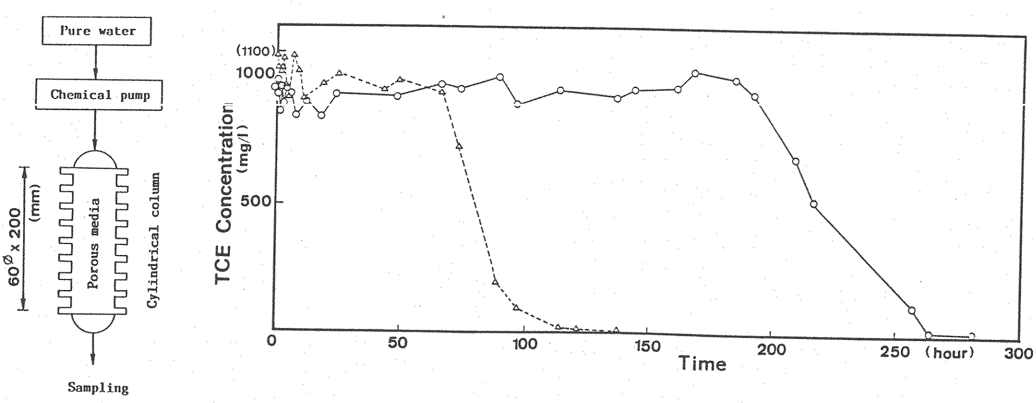


Fig.4 Leaching of Trichloroethylene from Soil, ○ : trichloroethylene 6g, △ : trichloroethylene 2g. Rainfall intensity and trichloroethylene leaching rate are 10mm/hr and about 70%, respectively, for both cases.

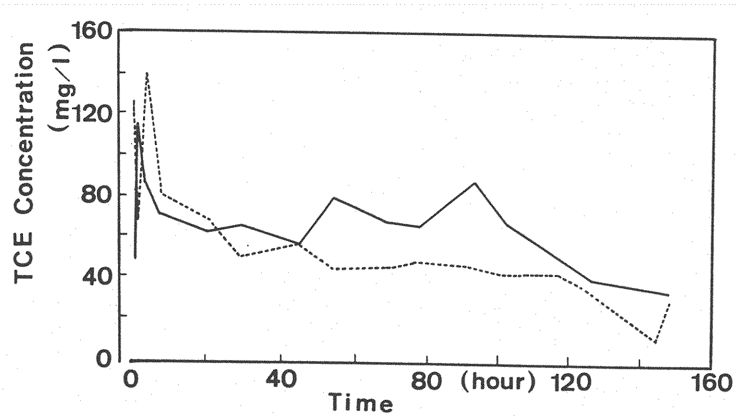


Fig.5 Leaching of Trichloroethylene by Groundwater, Weight of loaded trichloroethylene: 2g. Two loading methods are used: almost uniform loading over circular cross section (solid line) and loading only to center of circular cross section (dotted line).

Leaching of TCE in Two-Layered System Consisting of TCE and Water

The difference in the concentration of TCE leached by infiltrated rainwater and flowing groundwater was inferred to result from a difference in the contact time and contact area between water and TCE. To confirm this, a two-component layer consisting of undiluted TCE solution and water was formed in a rectangular glass tube 25cm long, 5cm wide and 5cm deep, and then the water in the upper layer was allowed to fall, followed by the determination of the concentration of the leached TCE(Muraoka et al.(12)). Results given in Fig.6 roughly indicate that the concentration of leached TCE decreases with increasing flow rate, or with decreasing contact time between water and TCE.

Essentially, organochlorines are highly insoluble in water. However, the tentative standards for drinking water have been set at extremely low values, and as a result, the solubility of TCE in soil and groundwater becomes several thousands of times as high as the standard values. In addition, organochlorines infiltrate more rapidly in soil than in water. Infiltration of undiluted solution of an organochlorine can cause serious groundwater pollution.

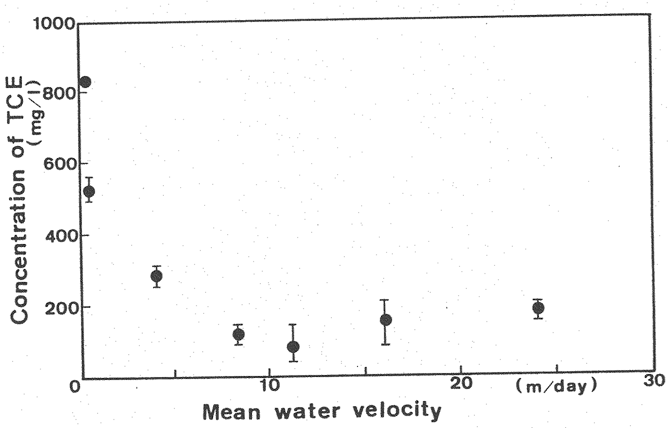


Fig.6 Leaching of Trichloroethylene in Trichloroethylene-Water Two-Layered System. Perpendicular stem for each experimental datum means the range of concentration of three water samples.

GROUNDWATER CONTAMINATION MONITORING BY SOIL GAS

Organochlorines including TCE are volatile. If these substances are contained in soil or groundwater, they will vaporize and diffuse in unsaturated soil, and reach the ground surface. The substances contained in the soil or groundwater can be identified indirectly by analyzing this soil gas.

There are two approaches to the analysis of soil gas: 1) analysis of soil gas directly sampled, and 2) use of an absorbent. Two practical methods for the second approach, using activated charcoal or Tenax, are described below.

Activated Charcoal

A detection tube made of grass and containing wire with charcoal attached to its surface is left in the surface soil (about 30cm deep) for two to three weeks. Then, the activated charcoal is taken out, purged, and analyzed with a pyrolysis mass detector, Which can identify gas components in the molecular weight range from 13 to 240. This technique is called "Finger Print Method" and begins to be used occasionally for the purpose of environment monitoring(Sakai(14)).

Using this detection tube, a survey was made in an area around spring water which had been found to be contaminated with tetrachloroethylene (PCE)(Muraoka et al.(12)). The surveyed area was on a mountain and ranged from 800m to 1,100m in altitude. Analysis of groundwater properties could not be made because there were no wells or surface water except for the spring water.

Fig.7 illustrates ion count contours developed by analyzing the mass spectra assuming that the counts for the molecular weight of 164 come from PCE. It can be seen from Fig.7 that PCE continuously distributes from the spring water point to a waste landfill site 1.5km to the north of the spring water point.

Tenax

We are currently in the process of developing a simple monitoring technique using soil gas as indicator. The technique employed is called "Tenax Method", which was originally devised by T. Mukai(Hirata et al.(5)). Soil gas in the surface soil is sampled through a glass tube (2.7mm diameter × 25mm) filled with Tenax (4g) so that organic compounds are absorbed on Tenax. This soil gas survey was carried out at the waste landfill site and spring water point. The Tenax tube was heated at 180°C and analysis was made with gas chromatograph ECD (analysis column DC550, 20% silicone coating). Results are shown in Fig.8, where the survey points are ranked into three classes in terms of the PCE concentration (ng in 1 ℓ of soil gas).

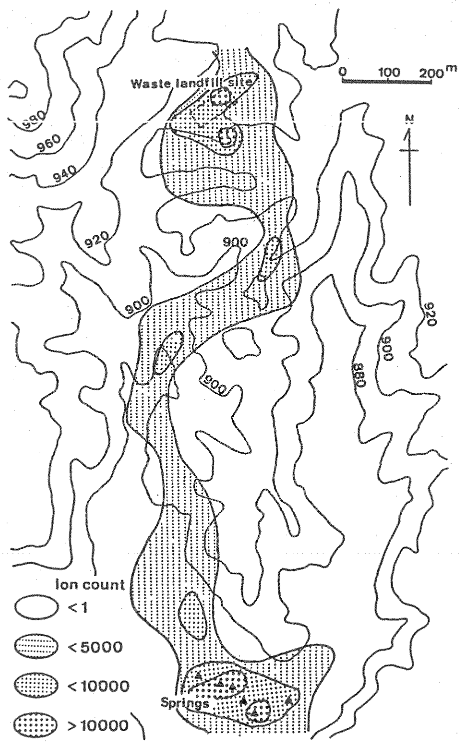


Fig.7 Survey of Soil Gas in Surface Soil by Means of Activated Charcoal. Spring sites are shown in mark ▲.

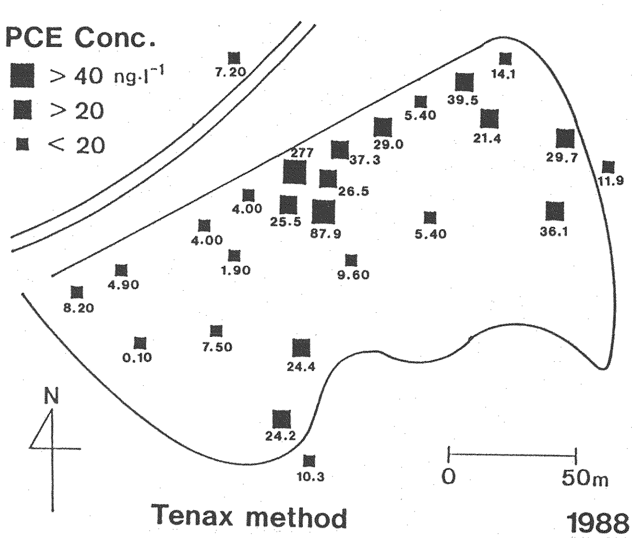


Fig.8 Distribution of Tetrachloroethylene in Soil Gas in Land Reclaimed with Incombustible Material

The soil gas concentration in surface soil is affected by such factors as the depth of the groundwater surface, the gas concentration in the groundwater, and physical properties of the soil. At present, there remain many problems to be solved to allow the the concentration and amount of substances in the ground to be determined from soil gas measurements. Since it is always possible to determine the relative differences in concentration among various points in a survey area, this can be a very helpful means of determining the spread of contaminants and identifying the contamination source.

FUTURE RESEARCH

Groundwater pollution with organochlorines has posed various problems, particularly because this type of pollution can occur in the groundwater sphere existing just around us and providing us with water sources. In the field of research, efforts should be made to achieve a variety of objectives for the contamination mechanism analysis, the development of water purification techniques, and the establishment of new laws and rules to prevent the enlargement of pollution from the present state.

Information currently available on the contamination mechanism is too little to provide a practical technique that is useful for water purification. It is still necessary to conduct basic research activities covering experiments with the leaching of organochlorines and observation of their behaviors near the groundwater surface. In any case, the contamination source has to be identified before taking measures for water purification. As a new method for this, it is hoped to establish the soil gas monitoring system.

In addition, the effects of water purification measures, such as the removal of contaminated soil, should be predicted accurately before carrying out the measures. Their evaluation, including the prediction of the diffusion of contaminants, has to rely on numerical simulation. We have made a numerical simulation study for groundwater in a contaminated area(Muraoka et al.(9)), but this could give only qualitative results. Thus, much more hydraulic information is required to solve problems involving groundwater pollution with organochlorine compounds.

ACKNOWLEDGEMENT

The present research work was partly supported by TORAY Science and Technology Grants, and the authors wish to thank the persons concerned of The TORAY Society for Promotion of Science.

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(Received January 5, 1990; revised September 6, 1990)