# Distribution of Nitrate Contamination from the Viewpoint of Recharge Year, Land Use History and Groundwater Flow System

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Abstract:

This study was carried out by using chlorofluorocarbons (CFCs) as tracers to examine the relationship between the distribution of high concentrations of $NO_3^-$ produced by an unlined disposal pit of animal waste and the site's land use history. From the results of investigation, CFC-11 is decreased by degradation in the nitrate attenuation zone of the study site. Recharge years using CFC-11 will make sites appear older than the actual values. Thus, detailed hydrogeological surveys should be taken into account estimating recharge years using CFCs. In the study site, recharge of high concentrations of $NO_3^-$ caused by leakage from the unlined disposal pit occurred between the late 1970s and about 1990. This result is consistent with the land use history of pig farming at this area, and it suggests that nitrate contamination from pig farming continues to have a large effect even now, more than 15 years after farming ceased.

Keywords: CFCs; recharge year; groundwater; unlined disposal pit; land use history; $NO_3^-$

## INTRODUCTION

The biggest cause of environmental problems accompanying livestock management is inappropriate disposal and storage of animal waste, such as exposed piles (*Nodumi* in Japanese) where animal waste in a solid form is simply piled up and left, and unlined disposal pits (*Subori* in Japanese) in which liquid animal waste is stored in a hole dug in the ground. In recent years, governmental legislation has come into effect, such as the Law on Promoting Proper Management and Use of Livestock Excreta (1999), and the number of farms that do not meet the control standards is decreasing. However, there are concerns that much inappropriate disposal and storage of animal waste was done in unlined disposal pits and exposed piles that have since been abandoned or backfilled, and so are still potential contaminant sources (Lee *et al*., 2009). Therefore, in dealing with groundwater contamination problems, such as assessing and restoring contaminated sites, it is essential to determine how long nitrogen remaining in abandoned or backfilled unlined disposal pits is retained.

The $^3H$ (Tritium) method of dating young groundwater has come to be widely used in Japan for estimating groundwater recharge years. However, recently, the $^3H$ concentration of precipitation in Japan has fallen to its natural level and the half-life of $^3H$ is short, $^3H$ has become ineffective as a tracer (Yabusaki *et al*., 2003). Because of this, methods for estimating young groundwater using chlorofluorocarbons (CFCs) have been proposed, and examples of their application are being collected, particularly in North America and Europe (IAEA, 2006). CFCs have properties that are very advantageous in tracers; for example, they are only produced artificially, are extremely stable, and the concentration of CFCs in the atmosphere increased almost

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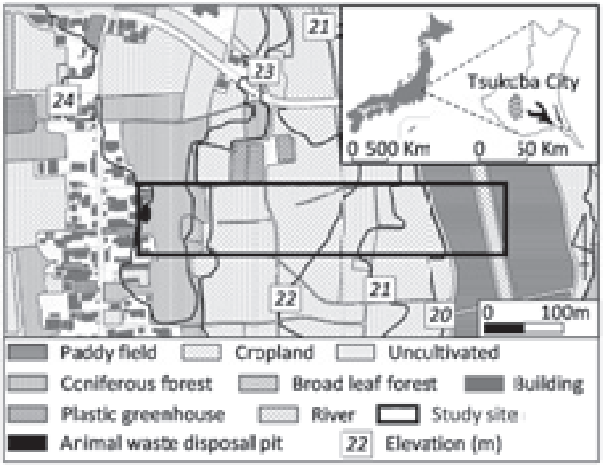


Fig. 1 Study site location and land use

monotonically until their legal regulation (Tsujimura *et al*., 2006).

Therefore, this study attempts to use CFCs to examine the relationship between the distribution of high concentrations of $NO_3^-$ caused by unlined disposal pits and local land use history.

## STUDY SITE

The study site is located in the Tsukuba upland about 15km west of the center of Tsukuba City, Ibaraki Prefecture, Japan, and is approximately 60km northeast of Tokyo (Fig. 1). Specifically, the study site, located in the Konomata district and slightly extending in the west-east direction, measures about 450 m × 100 m (about 4.5 ha). In the upstream western area of the study site and surrounding region, land use consists of forest, cropland, and paddy fields. The study site, in the central forested part of the upland, includes an abandoned unlined animal waste storage pit (9.7 m × 10.2 m × 2.5 m) associated with a pig farm. Even today, high concentrations of $NO_3^-$ (approximately 150 mg/L) are detected in the groundwater at approximately 50 m downstream from this pit (Lee *et al*., 2009).

## METHODS

### *Geological Conditions, Groundwater Flow, Water Quality, and δ*$^{15}$*N*

In order to understand the water quality distribution and groundwater flow system of the study site, wells

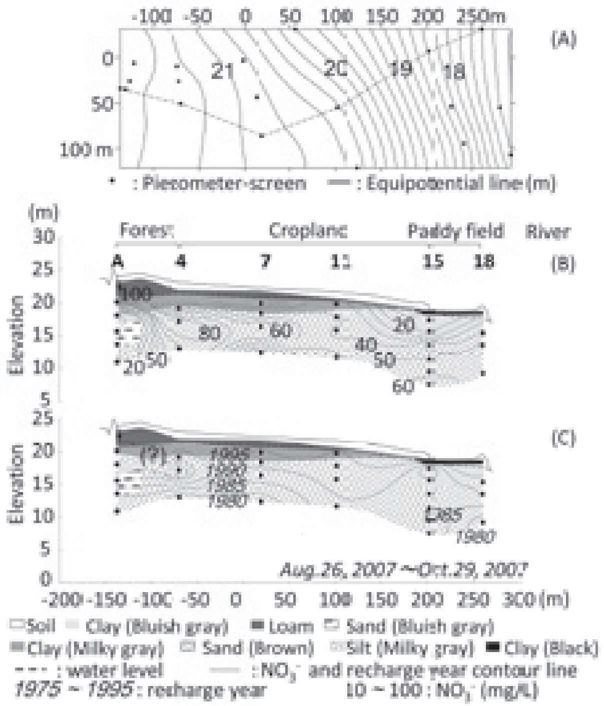


Fig. 2 (A) : Water table, (B) and (C) : $NO_3^-$ and recharge year of groundwater along cross section A-18

and piezometers were installed at a total of 19 points. Two to six piezometers were installed at each of point at depths from 2 m to 13 m (Fig. 2). In addition, in order to examine the geological conditions of the study site, soil cores were collected by boring and soil texture was determined. Ion chromatography (IC-7000, Yokogawa) was used in the water quality analyses, while an elemental analyzer (EA 1108, Fison) and a stable isotope mass spectrometer (DELTA PLUS, Thermo Finnigan) were used to measure $\delta^{15}N$.

### *Water Sampling and Analysis of CFCs*

In order to prevent contact with the atmosphere when collecting the groundwater samples, groundwater was pumped up using a tube pump, then placed in a 125 mL glass bottle inside a stainless steel container via a copper tube. After the pumped groundwater was allowed to overflow into the stainless steel container for a given period of time, the glass bottle was sealed under water and taken out (IAEA, 2006; Tsujimura *et al*, 2006; Asai *et al*., 2006). The groundwater samples were taken to a laboratory where the CFCs in the groundwater were isolated using a purge and trap method and measured by introduction into a gas chromatograph-electron capture detector (GC-ECD) (Bullister and Wesis, 1988; Tsujimura *et al*., 2006). CFCs were analyzed at depths from 2 m to 13 m in samples from points A, 4, 7, 11, 15, and 18 (a total of 25 piezometers), following the direction of groundwater flow (Fig. 2). Samples were collected during the period from August to October 2007.

### *Estimation of Recharge Year Using Piston Flow Model*

Generally, the Piston Flow Model (PFM) assumes that the atmospheric concentration at the time of recharge does not change during the flow process. On the other hand, the Exponential Model (EM) assumes that groundwater flowing into the aquifer mixes immediately with the groundwater in the aquifer. Although proportion of mixing rate in the groundwater flow differs depending on the hydrogeological conditions, and the PFM and EM combine in a complicated way. However, the PFM is considered to be more suitable for determining the time that nitrogen remaining in a disposal pit is retained because, in the case of groundwater contamination such as nitrate contamination, the contaminant flows in a plume shape.

In steady state conditions and with a non-radioactive tracer, the relation between the input and output tracer concentrations in groundwater may be formulated as a convolution integral:

$$C_{out}(t) = \int_0^\infty C_{in}(t-\tau)g(\tau)\,d\tau \qquad (1)$$

where $C_{in}$ and $C_{out}$ are input and output tracers concentrations, $\tau$ is the residence time, and $g(\tau)$ is the transit time distribution function (the system response or weighting function) of the mathematical model. (Zuber, 1986; Leibundgut *et al*., 2009).

In the PFM model, the flow lines are assumed to have the same transit time and hydrodynamic dispersion and diffusion are negligible. The transit time distribution function ($g(\tau)$) for PFM model is as follows (Maloszewski and Zuber, 2002; Leibundgut *et al*., 2009):

$$g(\tau) = \delta(\tau - T) \qquad (2)$$

## RESULTS AND DISCUSSION

### *Atmospheric Concentration of CFCs at the Study Site*

When estimating groundwater recharge years using CFCs, long-term input information on atmospheric CFCs at the study site is essential. Generally, atmospheric CFC concentration curves in the Northern Hemisphere Average Values (NHAV) published by the United State Geological Survey (USGS) CFC Laboratory are used for estimating recharge years using CFCs. However, although the distribution of the atmospheric concentration of CFCs is relatively uniform, high concentrations may occur locally in metropolitan areas and areas with a high density of industrial facilities. Japan is ranked third in the world for output of CFCs (IAEA, 2006). Therefore, the atmospheric concentrations of CFCs at Niihari, Tsuchiura City, Ibaraki Prefecture, located approximately 15km northeast of the study site in Tsukuba City, Ibaraki Prefecture (Ibaraki Prefecture, 1993 to 2007), were compared with the Northern Hemisphere Average Values (IAEA, 2006) (Fig. 3). At Niihari, the CFC-11 concentration was 7 % lower than the Northern Hemisphere Average Value, while the CFC-12 concentration was 14 % higher. So, the CFC-11 and CFC-12 values were corrected in this study to reflect the difference from the Northern Hemisphere Average Values. Consequently, the reproducibility of corrected results were improved by shifted towards the PFM line by mathematical model (Fig. 4).

Given this, it is possible that dating errors of 7 % to 14 % will occur when estimating recharge years using

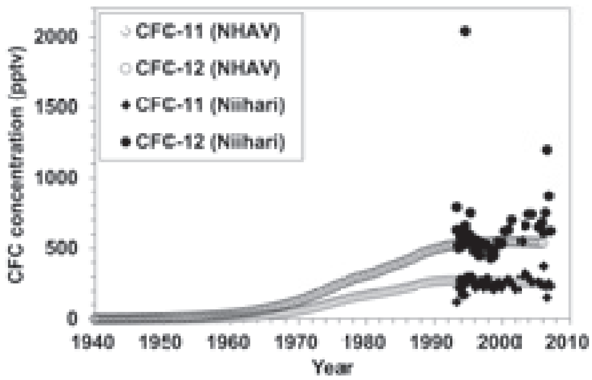


Fig. 3 Atmospheric concentrations of CFCs (Northern Hemisphere Average Values (NHAV) and Niihari (Japan))

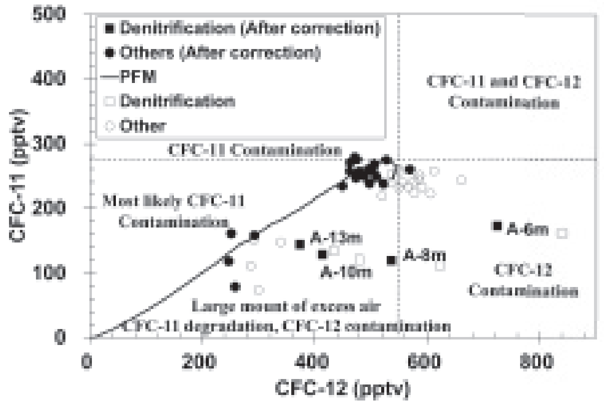


Fig. 4 Comparison of CFC-11 and CFC-12 concentrations and PFM model estimates

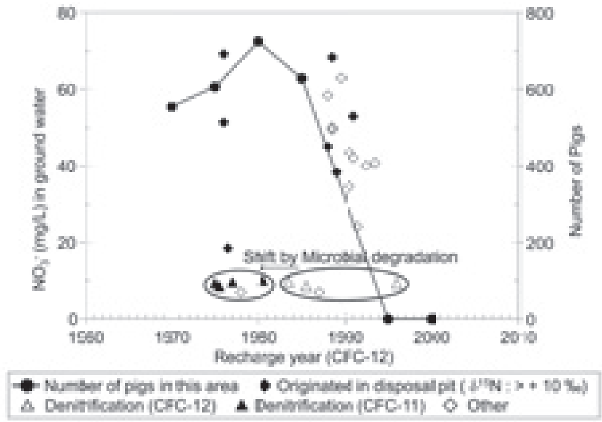


Fig. 5 Comparison of $NO_3^-$ concentrations and recharge years in groundwater with land use history

Northern Hemisphere Average Values, and long-term monitoring of atmospheric concentrations of CFCs at each site is needed to reduce the error.

### *Degradation of CFCs in a Reductive Environment*

A dramatic decrease in the concentration of CFC-11 was observed near a depth of 6 m (inside the bluish-gray clay) at Point A in the forest area (Fig. 4). Microbial degradation (denitrification) due to reductive environmental conditions has been reported in the vicinity of the bluish-gray clay at the study site, indicated by drastic decreases in $NO_3^-$ and ORP, and increases in $NO_3^-$, etc. (Lee *et al*., 2009). It is known that CFCs can be degraded by microbes under reductive environmental conditions, and CFC-11 is the most easily degraded, followed by CFC-13 and CFC-12 (Khalil and Rasmussen, 1989 ; Semprini *et al*., 1992). In other words, a groundwater recharge year estimated for a site with a reductive environment may be older than the actual recharge year due to degradation of CFC-11, etc. At this study site, CFC-11 concentrations drop significantly at depths of 6 m, 8 m, and 10 m at Point A, where the most denitrification occurs (Fig. 4). This means that CFC-11, which is more easily degradable in a reductive environment, is degrading faster than CFC-12. This can also be confirmed in Fig. 5. Points marked with ▲ indicate drops in CFC-11 due to microbial degradation under a reductive environment. Due to these drops, recharge years calculated using CFC-11 concentrations shift downward (Fig. 5). The maximum discrepancy in recharge year due to microbial degradation was 21 years at Point A, 8 m below the surface. Thus we see that not only $NO_3^-$ but also CFC-11 is degraded in the attenuation zone at the study site, which suggests that the recharge years calculated using CFC-11 will appear to be older than actual ones. Therefore, CFC-12, which is insusceptible to microbial degradation, was used to estimate recharge years at the study site, and the results were compared with the local land use history of livestock farming.

### *Consistency between Recharge Year Using CFCs and Livestock Farming Land Use History*

According to the Census of Agriculture and Forestry 2000 (Ministry of Agriculture, 2000), farms at the study site in Konomata, Tsukuba City, Ibaraki Prefecture had about 554 to 725 pigs (Table 1). The farmers went on pig farming for more than 25 years (from before 1970 until 1994), and more than 15 years have passed since it ceased (Table. 1). Fig. 5 presents the relationship

Table 1. Changes in livestock industry (pig farming) in Konomata (Ministry of Agriculture, 2000)

| Year | Number of pig farms (100 pigs or more) | Number of pigs |
|---|---|---|
| 1970 | 3 | 554 |
| 1975 | 3 | 606 |
| 1980 | 4 | 725 |
| 1985 | 2 | 629 |
| 1990 | 0 | 0 |
| 1995 | 0 | 0 |
| 2000 | 0 | 0 |

There has been no breeding of cows or chickens.

between recharge years and high concentrations of $NO_3^-$ by animal waste. Here, the stable nitrogen isotope ratio ($\delta^{15}N$) was used to select points affected by the animal wastes in the unlined disposal pit. $\delta^{15}N$ values of nitrate contamination sources range from -5 ‰ to +3 ‰ for chemical fertilizer and from +10 ‰ to +20 ‰ for animal waste. Because of this difference in $\delta^{15}N$ values, identification of contaminant sources is possible (Tase, 2003). From Fig. 5, we estimate that groundwater containing the high concentration of $NO_3^-$ (◆ marks indicate $\delta^{15}N \geqq +10$ ‰) due to the animal waste in the unlined disposal pit was recharged between late 1970s and around 1990, and we estimate that the $NO_3^-$ will flow out into the rivers with a residence time of about 30 years. However, while the number of pigs being farmed decreased starting in 1985, the high concentration of $NO_3^-$ (◆) caused by the unlined disposal pit does not start to decrease until around 1990, a gap of approximately 5 years (Fig. 5). The reasons are as follows: 1) a temporal gap until the high concentration of $NO_3^-$ from the unlined disposal pit leaches into the aquifer, 2) mixing from the ground surface with precipitation having a higher concentration of CFCs than the groundwater aside from the piston flow, and/or 3) an anthropogenic impact caused by animal waste itself, etc.

The high concentration of $NO_3^-$ from the unlined disposal pit flows from a depth of 4m at Point A, down through 6m at Points 4 and 7 and into deeper layers at Points 11 and 15, and upwards near 10m at Point 18. This shows a trend that is similar to groundwater flow mapped by recharge year (Fig. 2). As mentioned above, our results showed good agreement between the recharge year of the high concentration of $NO_3^-$ from the unlined disposal pit and the land use history of livestock farming. From above, we can also see that the distribution of high concentrations of $NO_3^-$ in the study site are consistent with the recharge year and land use history, estimation of recharge year using CFCs in shallow groundwater is considered to be valid.

## CONCLUSIONS

Comparing of atmospheric concentrations of CFCs at the study site in Ibaraki Prefecture with the Northern Hemisphere Average Values showed errors ranging from 7 % to 14 %. Long-term monitoring of atmospheric CFC concentrations at each study site is necessary in order to reduce this error. We compared the atmospheric concentrations of CFCs published in the Northern Hemisphere Average Values to those at the study site in Ibaraki Prefecture. Unfortunately, data was only available for the study site from 1993 to 2007. Therefore, we compared 1993 to 2007 and extrapolated the difference to previous years. It will be necessary in the future to develop a highly accurate correction model that takes into account CFC output before 1993 in the area around the study site.

In addition, in the nitrate attenuation zone of the study site, CFC-11 is degraded, which suggests that recharge years estimated using CFC-11 can be in error, appearing to be older than they are. Therefore, it is necessary to carry out detailed hydrogeological surveys to taken into account estimating recharge years using CFCs.

On the other hand, we estimated that the high concentration of $NO_3^-$ caused by the unlined animal waste disposal pit was recharged between late 1970s and around 1990. This is consistent with the land use history of livestock farming at the study site. This suggests that the high concentration of $NO_3^-$ in the study site still has a large effect on shallow groundwater and is a potential contaminant source even after approximately 15 years has passed since pig farming stopped, and urgent countermeasures are believed to be required.

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## SUPPLEMENTS

S 1. Recharge year estimates based on CFC-11 and CFC-12

S 1. Recharge year estimates based on CFC-11 and CFC-12

| Sample | CFC-11 (pptv) | CFC-12 (pptv) | After Correction | | Recharge Year | |
|---|---|---|---|---|---|---|
| | | | CFC-11(pptv) | CFC-12(pptv) | CFC-11(Year) | CFC-12(Year) |
| WA 4m | 1670 | 10449 | 1784 | 9006 | Contam. | Contam. |
| WA 6m | 162 | 840 | 173 | 724 | 1981 | Contam. |
| WA 8m | 112 | 623 | 120 | 537 | 1975 | 1996 |
| WA 10m | 120 | 480 | 129 | 413 | 1976 | 1986 |
| WA 13m | 135 | 433 | 144 | 374 | 1977 | 1984 |
| W4 4m | 240 | 536 | 257 | 462 | 1989 | 1988 |
| W4 6m | 243 | 661 | 259 | 570 | 1989 | Modern |
| W4 10m | 151 | 292 | 161 | 252 | 1979 | 1976 |
| W7 2m | 232 | 592 | 248 | 510 | 1988 | 1992 |
| W7 4m | 245 | 585 | 261 | 504 | 1989 | 1991 |
| W7 6m | 258 | 552 | 275 | 476 | 1995 | 1989 |
| W7 10m | 74 | 300 | 79 | 259 | 1972 | 1977 |
| W11 2m | 241 | 577 | 258 | 497 | 1989 | 1991 |
| W11 4m | 257 | 612 | 275 | 528 | 1995 | 1994 |
| W11 6m | 222 | 606 | 237 | 523 | 1987 | 1993 |
| W11 10m | 240 | 557 | 256 | 480 | 1989 | 1989 |
| W15 2m | 148 | 340 | 158 | 293 | 1979 | 1978 |
| W15 4m | 219 | 520 | 234 | 449 | 1987 | 1987 |
| W15 6m | 231 | 550 | 247 | 474 | 1988 | 1989 |
| W15 8m | 261 | 548 | 279 | 472 | 1995 | 1989 |
| W15 10m | 252 | 537 | 270 | 463 | 1991 | 1988 |
| W15 12m | 233 | 567 | 249 | 489 | 1988 | 1990 |
| W18 4m | 223 | 578 | 238 | 498 | 1987 | 1991 |
| W18 6m | 250 | 587 | 267 | 506 | 1991 | 1991 |
| W18 10m | 111 | 287 | 119 | 247 | 1975 | 1976 |

Modern : within the possible range of the modern atmosphere
Contam. : greater than maximum concentrations in the atmosphere

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# 涵養年代、汚染履歴、地下水流動系からみた硝酸性窒素汚染の分布

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キーワード：CFCs、涵養年代、地下水、素掘り、汚染履歴、$NO_3^-$

## 要　旨

本研究において、CFCs（Chlorofluorocarbons）を用いて調査を行い、素掘り廃棄ピットによる高濃度の$NO_3^-$の分布と汚染履歴（land use history）との関係について考察を行った。その結果、本研究対象地域の窒素還元場では、CFC－11も分解されており、CFC－11による涵養年代推定法では実際より古く見積もられることが示唆された。そのため、涵養年代を推定する際には、詳細な水文地質学的環境を調査する必要があることが明らかになった。また、素掘り廃棄ピットによる高濃度の$NO_3^-$は、1970年代後半から1990年前後にかけて涵養されたものと推定された。この結果は、本研究対象地域における畜産業による汚染履歴と整合性があり、養豚を止めてから約15年以上が経過している現在にも大きな影響を及ぼしていることが示唆される。

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