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Multiple tracer study in Horonobe, northern Hokkaido, Japan: 2. Depletion of chlorofluorocarbons (CFCs) estimated using $^3H/^3He$ index and lumped parameter models

Koki Kashiwaya [a,*], Takuma Hasegawa [a], Kotaro Nakata [a], Yuichi Tomioka [a], Takashi Mizuno [b]

[a] Nuclear Fuel Cycle Backend Research Center, Civil Engineering Research Laboratory, Central Research Institute of Electric Power Industry, 1646 Abiko, Chiba 270-1194, Japan
[b] Horonobe Underground Research Center, Japan Atomic Energy Agency, 432-2 Hokushin, Horonobe, Hokkaido 098-3224, Japan

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SUMMARY

The conservativeness of chlorofluorocarbons (CFC-12, CFC-11, and CFC-113) in an environment rich in organic carbon was evaluated using multiple tracer analyses and lumped parameter models (LPMs). Wells on a coastal plain in Horonobe, northern Hokkaido, Japan, were studied. The CFC concentrations in groundwater from 22 wells were measured, converted into atmospheric mixing ratios (CARs), and compared with estimated ratios (EARs) obtained from $^3H/^3He$ values and LPMs. The degree of CFC depletion was expressed as the percentage of the CAR relative to the EAR, and was less than 43% for CFC-12 and 28% for CFC-11 (but one well had unusual values). CFC-113 was depleted more than the other CFCs, and could not be detected in most wells. The CFC depletion mechanisms were different in each of the three well groups. Groundwater of northern Shimonuma wells (NSW) was oxic and oxidative, so CFC depletion in the NSW could be attributed to sorption by organic carbon in the lignite and peat in the aquifers. Groundwater of southern Shimonuma wells (SSW) was anoxic and reductive. The northerly SSW are supplied from the aquifer that supplies the most of the NSW, so CFC depletion in the SSW was caused by degradation under sulfate-reducing and methanogenic conditions, in addition to sorption by lignite in the northerly SSW. Gas stripping, contamination from a local source, and methane interfering with the CFC analysis were found in groundwater of Hamasato wells (HW). One well of HW was not affected by these problems, but the CFCs were depleted by microbial degradation. Assuming that the CFC depletion mechanisms follow first-order reaction kinetics, reaction rate constants of 2.7 y^{-1} for CFC-12 and 2.8 y^{-1} for CFC-11 were estimated. Microbial degradation, sorption, gas stripping of CFCs, and methane formation processes are enhanced in environments rich in organic carbon. Special attention is required when CFCs are used as transient tracers in such environments. The combination of multiple tracer analysis and LPMs allowed the degree of CFC depletion to be effectively quantified and the applicability of CFCs in groundwater flow systems to be evaluated.

1. Introduction

Chlorofluorocarbons (CFCs) are compounds with alkane backbones and with only fluorine and chlorine atom substituents (i.e., with no hydrogen atoms). CFCs are chemically and thermally stable, poorly flammable or nonflammable, and not very toxic (Siegemund et al., 1988). Commercial production of CFC-12, CFC-11, and CFC-113 started in 1930, 1936, and 1944 respectively (Plummer, 2007), and they were subsequently used for various purposes, including as refrigerants, as aerosol propellants, and as spraying and foam blowing agents (Siegemund et al., 1988). However, CFCs have been found to cause stratospheric ozone depletion (Cicerone et al., 1974; Molina and Rowland, 1974), so

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Abbreviations: BMM, binary mixing model; CAR, converted atmospheric mixing ratio; EAR, estimated atmospheric mixing ratio; EMM, exponential mixing model; EPM, exponential piston flow model; HW, Hamasato wells; LPM, lumped parameter model; NSW, northern Shimonuma wells; PFM, piston flow model; SSW, southern Shimonuma wells.

* Corresponding author at: Department of Urban Management, Graduate School of Engineering, Kyoto University, C1-2-214 Kyoto Daigaku Katsura, Nishikyo-ku, Kyoto 615-8540, Japan. Tel.: +81 75 383 3315; fax: +81 75 383 3318.

E-mail addresses: kashiwaya.koki.8a@kyoto-u.ac.jp (K. Kashiwaya), t-hase@criepi.denken.or.jp (T. Hasegawa), k-nakata@criepi.denken.or.jp (K. Nakata), tomioka@criepi.denken.or.jp (Y. Tomioka), mizuno.takashi@jaea.go.jp (T. Mizuno).

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their production, consumption, and trade were regulated by the Montreal Protocol. CFCs are also known to have greenhouse effects and, therefore, to contribute to global warming (Lacis et al., 1981; Lashof and Ahuja, 1990; Ramanathan, 1975). CFC concentrations in the atmosphere stopped rising and began to decline from the 1990s onward because of the regulations that were imposed.

Manufactured CFCs are emitted into the atmosphere and enter the water cycle (Plummer and Busenberg, 2000). CFCs in groundwater are now used regularly as transient tracers, and many successful applications of CFCs as transient tracers have been reported (e.g., Katz et al., 1995; Plummer et al., 1998a; Szabo et al., 1996). The conservativeness of CFCs is usually assumed in such applications (Happell et al., 2003), but the depletion of CFCs has been found in various environments, including aquifers (Cook et al., 1995; Happell et al., 2003; Hinsby et al., 2007; Horneman et al., 2008; Oster et al., 1996; Plummer et al., 1998a, 1998b; Sebol et al., 2007), surface water (Happell et al., 2003; Oster et al., 1996), and marine water (Shapiro et al., 1997). Cook et al. (1995) showed that the groundwater recharge rate estimated using CFC-113 (90 mm y^{-1}) was smaller than the rate estimated using a ^3H bomb pulse (150 mm y^{-1}) or CFC-12 (130 mm y^{-1}) because of the sorption of CFC-113 to materials in the aquifer. The recharge rate could not be determined using CFC-11 because the CFC-11 was degraded by microbes. Oster et al. (1996) compared the stabilities of CFC-12 and CFC-11 in anoxic environments. The CFC degradation rates in natural environments (groundwater and surface water) and laboratory experiments were found to range widely between 0.05 and 330 pmol L^{-1} y^{-1}, and the CFC-11 degradation rate was found to be approximately 10 times higher than the CFC-12 degradation rate. Shapiro et al. (1997) estimated CFC-12 and CFC-11 degradation rates in a super-anoxic water column in a fjord. Assuming that transport occurred through turbulent vertical mixing and assuming first-order degradation kinetics for the CFCs, the estimated degradation rates ranged between 0.01 and 0.03 y^{-1} for CFC-12 and between 6 and 9 y^{-1} for CFC-11. Sebol et al. (2007) found that CFC-12, CFC-11, and CFC-113 were completely degraded at a depth at which reduced sulfur (originating from pyrite) was oxidized by nitrate ions and dissolved oxygen. The estimated first-order degradation rates from that study were 0.3 y^{-1} for CFC-12, 0.7 y^{-1} for CFC-11, and 1.6 y^{-1} for CFC-113. Hinsby et al. (2007) demonstrated that CFC degradation can occur in the transition zone between aerobic and anaerobic groundwater in a shallow aquifer. The half-lives estimated from simulations in which first-order degradation kinetics was assumed were between a few months for CFC-11 and a few years for CFC-12 and CFC-113. Horneman et al. (2008) evaluated the stabilities of CFCs in an aquifer in a tropical climate. More than 95% of the CFCs were degraded in the anoxic groundwater, with an estimated residence time of more than 10 y. The CFC-12 and CFC-11 degradation rates were similar, approximately between 0.25 y^{-1} and 6 y^{-1}.

The degradation reactions of CFCs have been examined experimentally (Lesage et al., 1992; Lovley and Woodward, 1992; Sonier et al., 1994). Lesage et al. (1992) determined the degradation pathways of CFC-113 in biotic and abiotic environments. CFC-113 was found to be transformed into chlorotrifluoroethylene in a redox buffer under sulfate-reducing conditions. In contrast, CFC-113 was degraded to form HCFC-123a in a landfill leachate containing methanogenic bacteria and in a redox buffer containing hematin. The CFC-113 degradation rate was much higher in the landfill leachate than in the redox buffer. Lovley and Woodward (1992) demonstrated that CFC-12 and CFC-11 were degraded in different sediments and soils under anaerobic conditions but not under aerobic conditions. CFC-12 was degraded by active microbial metabolism, but CFC-11 was degraded by both microbial activity and nonenzymatic processes. Sonier et al. (1994) performed anaerobic incubation experiments using groundwater containing halogenated aliphatic compounds and a bacterial consortium, and they found that CFC-11 was degraded to form HCFC-21. The CFC-11 degradation mechanism was interpreted as being anaerobic dechlorination by sulfate-reducing bacteria.

The plausibility of interpreting hydrological systems using CFC measurements strongly depends on the conservativeness of the CFCs in the aquifer of interest. An understanding of the survivability of CFCs in a range of hydrological environments is required to improve the applicability of CFCs as environmental tracers. As is described later in detail, we conducted a multiple tracer study on 22 wells in a coastal plain in Horonobe, northern Hokkaido, Japan (Kashiwaya et al., 2014). A large part of the study area is occupied by a mire with a thick peat layer, and the groundwater at over half of the wells is supplied from an aquifer containing lignite. The mean groundwater residence time at each well was estimated and it is useful for estimating the CFC depletion rates and the mechanisms involved, and for evaluating the conservativeness of the CFCs in the organic-carbon-rich environment. In the study presented here, the CFC concentrations in groundwater from the same wells were measured and converted to atmospheric mixing ratios, and compared with the atmospheric mixing ratios estimated using lumped parameter models (LPMs, Zuber and Maloszewski, 2001) and a $^3H/^3He$ index. The CFC depletion mechanisms were assessed taking the hydrogeochemical environment and groundwater systems in the study area into account. The ultimate goal of this study is to evaluate the applicability of CFCs to investigations of hydrological systems in environments that are rich in organic carbon in boreal and humid regions.

2. Terrain, geological setting, and climatic conditions of the study area

Terrain and geological setting of the study area were described in Kashiwaya et al. (2014). They are summarized below together with climatic conditions of the study area. The study area was in Horonobe town, northern Hokkaido, Japan (Fig. 1). The terrain of the town can be broadly divided into an eastern mountainous area, a central hilly area, and an western coastal plain area. The Teshio Mountains (the northern part of the Ezo mountain range) form the mountainous area, and the highest point within the town is Mt. Isosannupuri-yama, which reaches 581 m. The central hilly area has an elevation of 100–250 m, and the Toikanbetsu tectonic basin (Oka, 1985) extends from the north-northeast to the south-southwest between the Teshio Mountains and the hilly area. The coastal plain faces the Sea of Japan in the west, and it is confined in the east by the western margin of the hilly area. The study area was located within the coastal plain, which is the middle part of the Teshio Plain (Fig. 1). A large area in the plain is occupied by the Sarobetsu Mire, which has an elevation of 1–8 m. This mire was formed as a result of the enclosure of the Sarobetsu Sea by a bar at the mouth of the bay and the aggradation of the coastal lake, and this was caused by sea level changes (Sakaguchi, 1961). Coastal lakes, such as Panke Pond and Penke Pond, can still be found in the central part of the Sarobetsu Mire. Sand dunes extend through the study area 1.5–2 km from the Sea of Japan shore, from the north-northwest to the south-southeast (Mitani, 1981).

The study area has been classified as having a Dfb Köppen–Geiger climate (Miyamoto, 2009). The climate statistics for the Toyotomi observation point (the nearest observation point in the Japan Meteorological Agency's Automated Meteorological Data Acquisition System (AMeDAS)) for 1981–2010 can be summarized as: 1072.5 mm mean annual precipitation; an average temperature of 6.1 °C; a highest average monthly temperature of 23.7 °C in August; a lowest average monthly temperature of −12 °C in February; and an annual accumulation of 764 cm of snow.