Multiple evaluations of the removal of pollutants in road runoff by soil infiltration

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ABSTRACT

Groundwater replenishment by infiltration of road runoff is expected to be a promising option for ensuring a sustainable urban water cycle. In this study, we performed a soil infiltration column test using artificial road runoff equivalent to approximately 11–12 years of rainfall to evaluate the removal of pollutants by using various chemical analyses and bioassay tests. These results indicated that soil infiltration treatment works effectively to remove most of the pollutants such as organic matter (chemical oxygen demand (COD_{Mn}) and dissolved organic carbon (DOC)), P species, polycyclic aromatic hydrocarbons (PAHs), numerous heavy metals and oestrogenic activities. Bioassay tests, including algal growth inhibition test, Microtox® and mutagen formation potential (MFP) test, also revealed effective removal of toxicities by the soils. However, limited amounts of NO_3, Mn, Ni, alkaline earth metals, perfluorooctane sulphonate (PFOS) and perfluorooctane sulphonamide (FOSA) were removed by the soils and they possibly reach the groundwater and cause contamination.

1. Introduction

In order to ensure a sustainable urban water cycle, it is necessary to establish a self-regulated urban water recycle and reuse system. In particular, groundwater replenishment has been expected as a strategy for water management. Infiltration of road runoff and wastewater is a promising option for groundwater replenishment.

Road runoff is known to contain several pollutants such as heavy metals and polycyclic aromatic hydrocarbons (PAHs) (Striebel et al., 1994; Pitt et al., 1995; Sansalone and Buchberger, 1997; Kumata et al., 2000; Murakami et al., 2004; Han et al., 2006). These pollutants are derived from vehicle exhaust emission, vehicle tyres, asphalt pavement, paint markers and so on and are diffusely accumulated on road dust (Murakami et al., 2005, 2007). Additionally, other

pollutants such as perfluorooctane sulphonate (PFOS), which is one of the perfluorinated surfactants (PFSs), might be also present in the runoff because these pollutants are transported via the atmosphere and are widely distributed in dust (Sasaki et al., 2003). Heavy metals, PAHs and PFOS are acutely and chronically toxic and carcinogenic compounds and produce adverse effects on humans and aquatic ecosystems (Enserink et al., 1991; Maltby et al., 1995; Nakayama et al., 2005). PAHs and heavy metals in runoff are present in both particulate and dissolved phases. Sansalone and Buchberger (1997) observed that the event mean concentrations of Cu, Zn and Cd in road runoff exceeded the Ohio EPA surface water quality discharge standards for both total and dissolved fractions. In their study, the dissolved event mean concentration of Pb ranged from 13 to 21 µg/L, which exceeded the upper limit specified in guidelines for drinking water quality (10 µg/L in Japanese and WHO guidelines). PAHs, particularly those containing more than 3 aromatic rings, were mostly transported with particles in road runoff (Kumata et al., 2000). Maltby et al. (1995) implied that particle-bound PAHs in road runoff were the pollutants responsible for toxicity to the benthic amphipod. Evaluation of toxicities by bioassay tests also highlighted significant toxicities of road dust and runoff. Genotoxicity and oestrogenic activities were determined in road dust and increased with traffic activities (Degirmenci et al., 2000). Marsalek et al. (1999) showed that the highest frequencies of severe and moderate toxicity were found at highway runoff sites by using a battery of 7 bioassays, whereas the frequencies of combined sewer overflow toxicity were considerably lower. These pollutants are a major barrier to the reuse of road runoff.

Infiltration facilities are expected to serve as a prospective system for groundwater replenishment, wherein road runoff can be infiltrated to groundwater (Furumai et al., 2005). For example, the infiltration facilities constructed in Tokyo continue to contribute efficiently to inundation control and groundwater replenishment even after 2 decades of operation (Furumai et al., 2005). Further, it is reported that some of the nonpoint pollutants could be trapped during infiltration (Mikkelsen et al., 1996; Dechesne et al., 2004; Murakami et al., 2007). Mikkelsen et al. (1996) revealed that in the infiltration systems with 12–45 years of operation in Switzerland, the content of pollutants such as heavy metals and PAHs decreased rapidly to background levels within depths of less than 1.5 m; this suggested that soil and runoff sludge acted as sorbent. This accumulation onto surface sediments/soils within or below infiltration facilities was reported by several researchers (Dechesne et al., 2004; Murakami et al., 2007). On the other hand, a potential concern related to groundwater contamination through infiltration facilities has also been pointed out based on field investigations (Mason et al., 1999). These field investigations have disadvantages with regard to evaluation of changes in the removal efficiencies of pollutants in long-term operations.

Compared to field investigations, bench-scale experiments such as soil infiltration column tests are useful methods to assess the removal efficiencies and mobility of pollutants. By using artificial road runoff, Kimura et al. (2003) evaluated a porous polypropylene treatment for highway runoff and obtained approximately 50% of removal efficiencies for

suspended solids and chemical oxygen demand (COD_{Cr}). Legret et al. (2005) applied both static batch and column tests for leaching of heavy metals and PAHs from reclaimed asphalt pavements. They found that pollutant concentrations in leachates from batch and column tests in the late stage were generally below the detection limits and European Community (EC) limits for drinking water.

However, limited research has been carried out on multiple evaluation of the removal of pollutants by using comprehensive chemical analyses and bioassay tests. We performed infiltration column tests to evaluate the removal of pollutants in treated wastewater by using various chemical analyses and bioassay tests (Shinohara et al., 2006; Nakada et al., 2007). In this study, artificial road runoff was prepared and passed through soil columns. The aim of this study was to evaluate the removal efficiencies of pollutants in road runoff during soil infiltration by using multiple chemical analyses and bioassay tests and to determine the pollutants that possibly reach the groundwater.

2.　　Materials and methods

2.1.　　Soil column test

Detailed descriptions of columns and soils used for the test have been reported elsewhere (Nakada et al., 2007). Briefly, soil samples were collected from the typical loamy layer in a park in Kanto district, Tokyo, at depths of 90–120 cm from the surface. The soil samples were air-dried and sieved with 75- and 2000-µm mesh screens to obtain 75–2000-µm soil particles. The sieved soil was then packed in 3 columns to a depth of either 20 or 50 cm (each weighing 5 and 12.5 kg, respectively). One 20-cm-deep and two 50-cm-deep soil columns were prepared.

Artificial road runoff was prepared using road dust/sediments and groundwater. Road dust and sediments in rainwater drainage pits were collected on 29 November 2005, at Metropolitan Expressways (Expressway No. 9 Fukagawa Line and No. 11 Daiba Line; traffic volume: 59,397–67,446 vehicles/day (Japan Society of Traffic Engineers, 2001)) by a road sweeper from the Metropolitan Expressway Company Limited. The collected road dust and sediments were air-dried and sieved through a 2000-µm mesh screen to remove large stones. Road dust/sediments and groundwater, which was collected from 120 m below the ground at Ohigawa, Shida, Shizuoka, were mixed at an L/S ratio of 25 L/kg and stirred for 6 h at a speed of 250 rpm at 20 °C in the dark. The supernatant obtained after more than 15 h of settling was regarded as the artificial road runoff.

Prior to the soil column test using the artificial road runoff, groundwater was fed into the columns at a flow rate of 5 mm/h (2.6 mL/min) for 14–15 days in order to release water-soluble pollutants accumulated in the soils. The artificial road runoff was then fed into the columns in a down-flow mode at a flow rate of 10 mm/h (1680 mm/week) under 2 different flow conditions, namely, continuous and intermittent. The flow volume under the continuous condition in 1 week of test mostly corresponded to 1 year of rainfall in Japan. The artificial road runoff was fed into both the 20- and 50-cm-deep soil columns

for a total of 79 days under the continuous flow condition. Additionally, the artificial road runoff was passed only through the 50-cm-deep soil column every alternate day for a total of 157 days under the intermittent flow condition. Taken together, the artificial road runoff equivalent to approximately 11–12 years of rainfall was passed through the soils. Effluent samples from the columns were collected after 2, 9, 16, 23, 30, 37, 44, 51, 58, 65, 72 and 79 days under the continuous condition and 3, 17, 31, 45, 59, 73, 87, 101, 115, 129, 143 and 157 days under the intermittent condition. The artificial road runoff was typically analysed 3 times (2, 72 and 143 days) for measuring all chemical analyses parameters, except PAHs, and some bioassay tests (yeast oestrogen screen (YES) assay, algal growth inhibition (AGI) test and Microtox® acute toxicity test); 2 times (2 and 72 days) for measuring PAHs; and 4 times (2, 72, 143 and 157 days) for bioassay tests. The soil columns were sectioned at 5-cm-depth intervals after the tests. The soils were analysed for total C (T-C), total N (T-N), total P (T-P) and PAHs before and after the column test. The column test was conducted at a constant room temperature (20 °C) in the dark.

2.2. Chemical analyses

The pH, electrical conductivity (EC), COD_{Mn}, dissolved organic carbon (DOC), biochemical oxygen demand (BOD), N species, P species, metals (Be, Mg, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Mo, Sb, Ba, Pb and V) and PFSs (PFOS and perfluorooctane sulphonamide (FOSA)) in the artificial road runoff water (the column influent) and the infiltrated water (the column effluent) samples were measured after filtering the water samples through a GF/F glass fibre filter (Whatman, pore size: 0.7 μm). Samples for PAH measurement were filtered through a GC50 glass fibre filter (Advantec, pore size: 0.5 μm).

COD_{Mn}, DOC, BOD, N species, P species and metals in the filtrates were measured using the standard method JIS K0102 (Japanese Standards Association, 1998). DOC was determined using a total organic carbon analyser (Shimadzu TOC-5000A). Nitrogen species and P species were measured using a spectrophotometer (Hitachi U-2000). Metals were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) (Agilent 4500). T-C and T-N in the soil samples were measured by the CHN Elemental Analyser (Elementar Vario EL), and T-P was measured using the spectrophotometer after the decomposition.

Detailed descriptions of PAH measurements have been reported elsewhere (Kose et al., in press). Briefly, PAHs in the filtrates were concentrated by a factor of 10,000 using C-18 type carrier solid-phase extraction discs (capacity: 15 mg, 3 M Empore). PAHs adsorbed on the disc were eluted with 5 mL of dichloromethane. PAHs in the soils were extracted with 50% (v/v) toluene in methanol by pressurized solvent extraction (ASE-200, Dionex). The eluate and extract were dried, redissolved in 1 mL of n-hexane and then purified by the solid-phase extraction cartridge Sep-Pak Plus Silica (mass of adsorbent: 360 mg, Waters). The fractions containing PAHs were eluted with 3 mL of 30% (v/v) dichloromethane in n-hexane after the saturated hydrocarbon fraction was removed with 3 mL of n-hexane. Phenanthrene-d_{10} was added as an internal injection standard, and the fractions were then

concentrated and redissolved in 100 μL of n-hexane. The samples were analysed for PAHs by GC–MS QP2010 (Shimadzu) integrated with GC-20A gas chromatograph equipped with a DB-5MS capillary column (0.25 mm i.d. × 30 mL with 0.25 μm liquid phase, J&W Scientific) in the selected ion monitoring mode. The quantified PAHs were as follows: fluorene, phenanthrene, anthracene, 9-methylphenanthrene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[g,h,i]perylene. Reproducibility and recovery rates of PAHs were preliminarily confirmed by spiking surrogate standards (deuterated PAHs with 3–6 rings: fluorene-d_{10}, anthracene-d_{10}, fluoranthene-d_{10}, benzo(a)anthracene-d_{12}, benzo(a)pyrene-d_{12} and dibenzo(a,h) anthracene-d_{14}) into water and solid samples ($n = 5$ for both water and solid samples). Relative standard deviation (RSD) of individual deuterated PAH spiked into water and solid samples ranged from 3% to 11% and from 6% to 13%, respectively. Recovery rates for water and solid samples ranged from 87% to 99% and from 84% to 95%, respectively.

The PFSs in the filtrates were concentrated by a factor of 1000 using solid-phase extraction. Aliquots of 500–1000 mL of samples were passed through the Sep-Pak Plus tC18 cartridges (mass of adsorbent: 900 mg, Waters) preconditioned with 20 mL of methanol and 10 mL of distilled water. A flow rate of less than 10 mL/min was maintained. The cartridges were then washed with 7 mL of 30% (v/v) methanol in distilled water, followed by a wash with 7 mL of 55% (v/v) methanol in distilled water that was acidified with 4 M HCl to pH 2.0–2.5. The target compounds were eluted with 20 mL of methanol. The eluate was concentrated to 0.5–1 mL. PFSs were analysed by LC–MS/MS (Agilent 1100 series and TSQ Quantum) in the electrospray negative ionization mode. Aliquots of 10 μL of the extract were injected onto a Zorbax Rx-C8 column (4.6 × 150 mm, 5 μm, Agilent). A gradient mobile phase of 0.5 mM ammonium acetate in distilled water and 0.5 mM ammonium acetate in acetonitrile was used. At a flow rate of 0.3 mL/min, the mobile phase gradient was ramped from 20% to 100% of 0.5 mM ammonium acetate in acetonitrile in 5 min, maintained at 100% of 0.5 mM ammonium acetate in acetonitrile for 11 min and ramped down to 20% of 0.5 mM ammonium acetate in acetonitrile. The capillary temperature was maintained at 350 °C. Ions were monitored using the selected reaction monitoring mode for a parent ion at m/z 499 and product ions at m/z 80 and 99 for PFOS and a parent ion at m/z 498 and product ions at m/z 78 and 478 for FOSA. The reproducibility and recovery rates were confirmed using secondary effluent from a wastewater treatment plant. RSD ($n = 4$) was 4% for both PFSs. Recovery rates of PFOS and FOSA spiked into the wastewater samples ($n = 4$) were 109% and 96%, respectively.

The detection limits were as follows: ~0.5 mg/L for COD_{Mn} and BOD, 0.2 mg/L for DOC, ~0.01 mg N/L for N species, and ~0.001 mg P/L for P species, ~3 ng/L for Be, ~0.1 μg/L for Co; ~0.3 μg/L for Cr, Ni, As, Sb and Pb, ~1 μg/L for V, ~3 μg/L for Al, Mn, Cu, Zn, Sr, Mo and Ba, ~30 μg/L for Mg, ~50 μg/L for Fe, ~0.2 ng/L for individual PAHs, and ~0.1 ng/L for PFOS and FOSA. Linear regressions of calibration standards (3–6 point calibrations) were as follows: R^2 values of >0.995 for DOC, >0.990 for N species, >0.995 for P species, >0.995 for

all metals, >0.970 (normally >0.985) for PAHs and >0.990 for PFSs.

2.3.   Bioassay tests

Four different bioassay tests (YES assay, AGI test, Microtox® acute toxicity test and mutagen formation potential (MFP) test) were performed in this study. Ascorbic acid at a final concentration of 1 g/L was added to the samples in all bioassay tests, except MFP. The samples for all bioassay tests, except MFP, were filtered through GF/B glass fibre filters (Whatman, pore size: 1.0 μm). At a flow rate of 10 mL/min, aliquots of 1000 mL of the filtrates were passed through an Oasis HLB cartridge (mass of adsorbent: 500 mg, Waters) preconditioned with 10 mL of methanol and 10 mL of distilled water. Components adsorbed on the cartridge were eluted by 10 mL of methanol. The eluate was dried under a nitrogen gas stream and then redissolved in dimethyl sulphoxide. These solutions were termed as 'concentrated sample'. The concentration factors were 10,000. The remaining aliquots of the filtrates were further filtered using membrane filters (Advantec, pore size: 0.45 and 0.2 μm) and termed as 'nonconcentrated samples'. YES assay was applied only to the concentrated samples, AGI test was applied only to the nonconcentrated samples and Microtox® test was applied to both samples. Samples for MFP were filtered through GA-100 glass fibre filters (Advantec, pore size: 1.0 μm). The test method for each assay is described below.

To evaluate oestrogenic activity of hydrophobic pollutants, the concentrated samples were subjected to YES assay using a DNA recombinant yeast strain. The yeast strain was kindly gifted by Prof. Sumpter, Brunel University, UK. This strain carries the human oestrogen receptor α. The assay was performed as described by Routledge and Sumpter (1996) with some minor modifications (Nakada et al., 2006). Oestrogenic activity was calculated as a relative value for the activity of 17β-estradiol, which is a positive control and was included in each experiment.

For AGI test, the cultured algae (*Pseudokirchneriella subcapitata* NIES-35) were exposed to the nonconcentrated samples in a 96-well microplate according to the standard method (Blaise et al., 1986) with minor modifications (Yamashita et al., 2006). A dilution series of the nonconcentrated samples (maximum concentration 83.3%) was prepared for the exposure test by serial 1:1 dilution of the samples with the culture medium for up to 5 steps. After the test, the AGI rate was calculated from the area under the algal growth curve, while the EC_{50} value was calculated based on the relationship between the sample concentration and the AGI rate.

To demonstrate toxicities to bacteria that are present in the bottom layer of the ecosystem, both concentrated and nonconcentrated samples were subjected to the Microtox® acute toxicity test. The test was conducted according to the 'Microtox® Acute Toxicity Basic Test Procedures' provided with the Microtox® equipment. In brief, the luminescent marine bacterium *Vibro fischeri* was exposed to serial dilutions of concentrated and nonconcentrated samples for 5 and 15 min. Light production after 5 and 15 min of exposure was measured using a photometer designed to the Microtox® test (Microtox® Model 500, Azur Environmental). The maximum

exposure concentrations of concentrated and nonconcentrated samples were 1800% and 81.9%, respectively. The EC_{50} value (concentration required to inhibit 50% of light production) was calculated by comparing the result of the test samples with that of the control. The computer program 'Microtox® Omni™ Software' (Azur Environmental) was used to calculate EC_{50} values. Among the different protocols in the software, we applied '81.9% Basic test protocol' to the nonconcentrated samples and '90% Basic test for pure compounds' to the concentrated samples.

Mutagenicity of the chlorinated water samples (MFP) was measured as the index of genotoxicity. MFP is useful to evaluate the quality of drinking water that may contain pollutants capable of forming mutagens when chlorinated under the conditions used in water purification processes (Takanashi et al., 2001). After performing the filtration of water samples as described above, chlorination and concentration procedures for measuring MFP were carried out according to the method proposed by Takanashi et al. (2001). Mutagens present in aliquots of 900 mL of the chlorinated water samples were concentrated by a factor of 1000 with the adsorbent CSP-800 (mass of adsorbent: 420 mg, Waters) at a flow rate of 30 mL/min and dissolved in dimethyl sulphoxide. The mutagenic activity of the dimethyl sulphoxide solution was examined by the Ames mutagenicity assay using *Salmonella typhimurium* strain TA100 without S9 mix (TA100-S9). The TA100-S9 condition was employed because high mutagenicity has generally been detected in chlorinated water samples under this condition (Takanashi et al., 2001). The mutagenicity of the water samples was evaluated as net revertant colonies per litre of water sample.
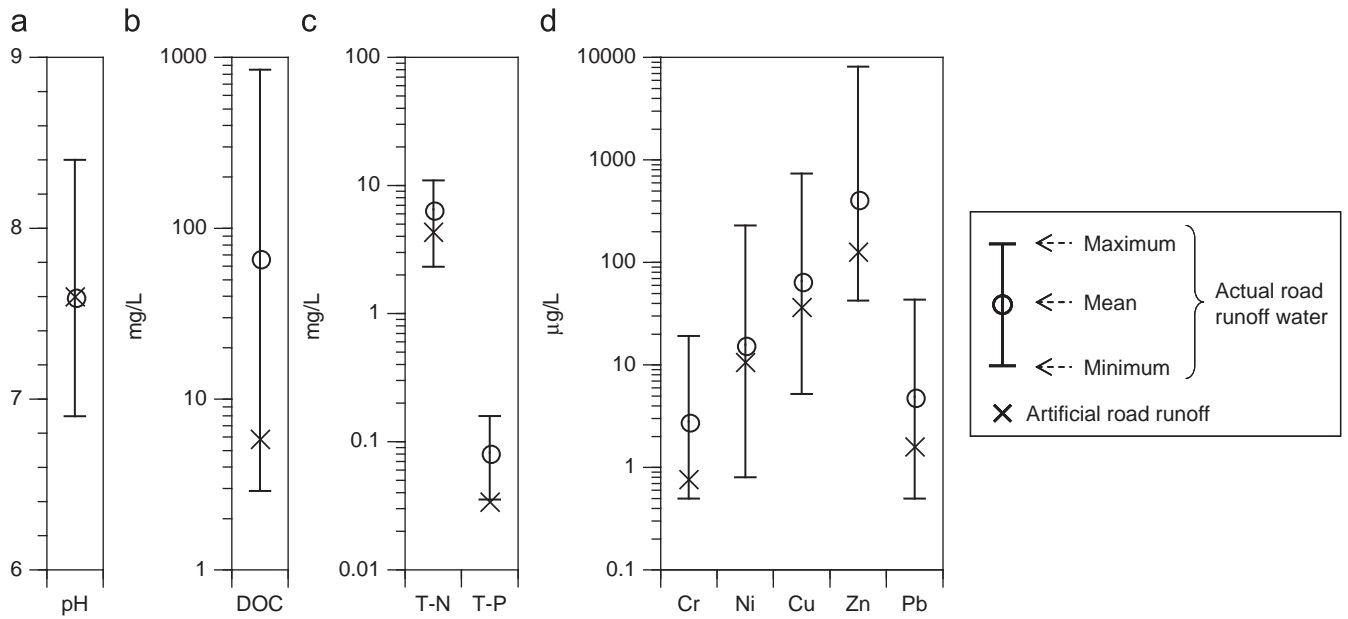
3.   Results and discussion

3.1.   Comparison of chemical parameters (pH, DOC, T-N, T-P and heavy metals) in dissolved phases between the artificial and actual road runoff water

To demonstrate the validity of the artificial road runoff water used in this study, we compared the values of chemical parameters (pH, DOC, T-N, T-P and heavy metals) of the artificial road runoff water in the dissolved phases with those in the actual road runoff water reported in the literature (Pitt et al., 1995; Han et al., 2006; Shinya, 2007). PAHs and PFSs were not compared due to the limited data. Fig. 1(a–d) shows the mean values of pH, DOC, T-N, T-P and heavy metals in the dissolved phases of the artificial road runoff water and the ranges reported in the literature. The values of pH, DOC, T-N, T-P and heavy metals in the artificial road runoff water were within the ranges reported in the literature for the actual road runoff water, although the concentrations of DOC, T-P, Cr, Zn and Pb in the artificial road runoff water were relatively low. Therefore, the artificial road runoff water prepared from road dust/sediments and groundwater could be regarded as valid.

3.2.   pH, EC and organic matter

Fig. 2(a–c) shows the behaviour of COD_{Mn}, DOC and BOD in the artificial road runoff water and infiltrated water during

Fig. 1 – Comparison of chemical parameters ((a) pH, (b) DOC, (c) T-N, T-P and (d) heavy metals) in dissolved phases between the artificial and actual road runoff water. The following values for actual road runoff water were obtained from the literature: pH, *n* (total number of events) = 6 (Pitt et al., 1995); DOC and heavy metals, *n* = 47–62 (Han et al., 2006); T-N and T-P, *n* = 8, calculated from the event mean total (dissolved+particulate) concentrations and mean values of dissolved fractions (Shinya, 2007).
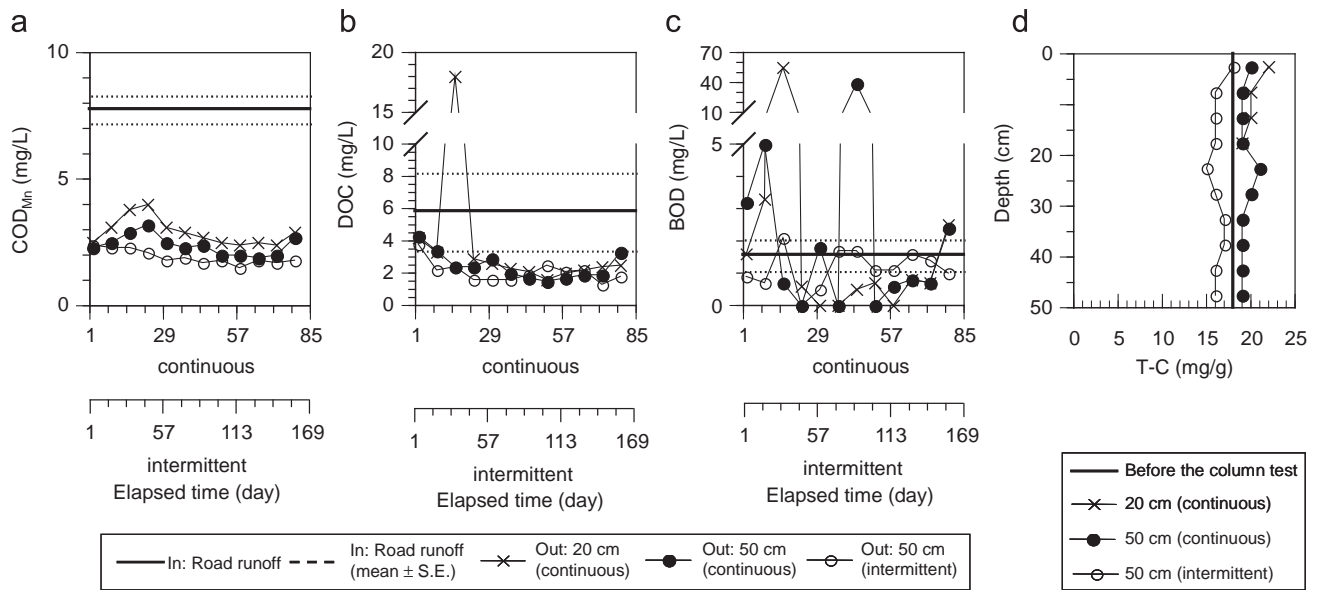
Fig. 2 – Behaviour of (a) COD_{Mn}, (b) DOC and (c) BOD in the artificial road runoff water and infiltrated water and (d) the depth distribution of T-C contents in the soils.

the soil column tests. The behaviour of pH and EC is shown in Fig. S1. In the figure, the *x*-axis is shown in 2 different time scales for continuous and intermittent conditions in order to conform to the flow volume scale.

The concentrations of COD_{Mn} and DOC in the infiltrated water were lower than those in the artificial road runoff water. This indicated that COD_{Mn} and DOC were significantly removed by the soils. A repeated-measures analysis of

variance (ANOVA) test with Bonferroni correction showed that there were significant differences in the behaviour of COD_{Mn} ($P < 0.05$) and, thus, in removal efficiencies among 3 columns. The cumulative whole stage removal efficiencies (overall removal efficiencies) were as follows: COD_{Mn}, 62% for the 20-cm column (continuous) < 69% for the 50-cm column (continuous) < 75% for the 50-cm column (intermittent). Similar tendencies were observed in overall removal

efficiencies of DOC as follows: 33% for the 20-cm column (continuous), 60% for the 50-cm column (continuous) and 65% for the 50-cm column (intermittent). The highest removal efficiencies for COD_{Mn} and DOC were achieved in the 50-cm column under the intermittent condition, whereas the removal efficiencies were the lowest in the 20-cm column. However, the organic carbon content in the 50-cm-deep soil column under the intermittent condition decreased after the test, as shown in Fig. 2(d). Since the test was performed in the dark, photodegradation did not likely occur. This suggested that the repetition of wet and dry conditions facilitated the biodegradation and/or evaporation of organic matter. This warrants further investigations on microbial community variations along with the identification of key microorganisms to substantiate biodegradation during the process.

In contrast to the significant removal of COD_{Mn} and DOC, the removal efficiency of BOD varied largely, suggesting that the soil infiltration treatment is not effective for BOD removal. In the soil infiltration treatment using the road runoff, the removal efficiency of BOD was lower than that of COD_{Mn} and DOC. This result was consistent with that using the treated wastewater (Nakada et al., 2007).

3.3. Nitrogen and P species

Fig. 3(a–f) shows the behaviour of N and P species. The speciation of N dynamically changed during the test; this indicated that bioactivation caused nitrification. Although there was sufficient removal of T-P and PO_4-P (overall removal efficiencies for 3 columns: T-P, 95%; PO_4-P, 99–100%), the removal of T-N by the soils was limited (6–13%). A repeated-measures ANOVA test with Bonferroni correction showed that no significant differences were observed in the behaviour of T-N and T-P among the 3 columns ($P > 0.05$ for both). As shown in Fig. S2, slight removal of T-N and significant removal of T-P were supported by the depth distribution of T-N and T-P contents in the soils. T-N and T-P contents in the soils were increased after the test, irrespective of the column type. However, as shown in Fig. 3(d), the concentration of NO_3-N in the infiltrated water was comparable to or higher than that in the artificial road runoff water. These results were also consistent with the observation noted in the soil infiltration treatment using treated wastewater (Nakada et al., 2007). This implies that NO_3 was not removed by the soils and could finally reach the groundwater.
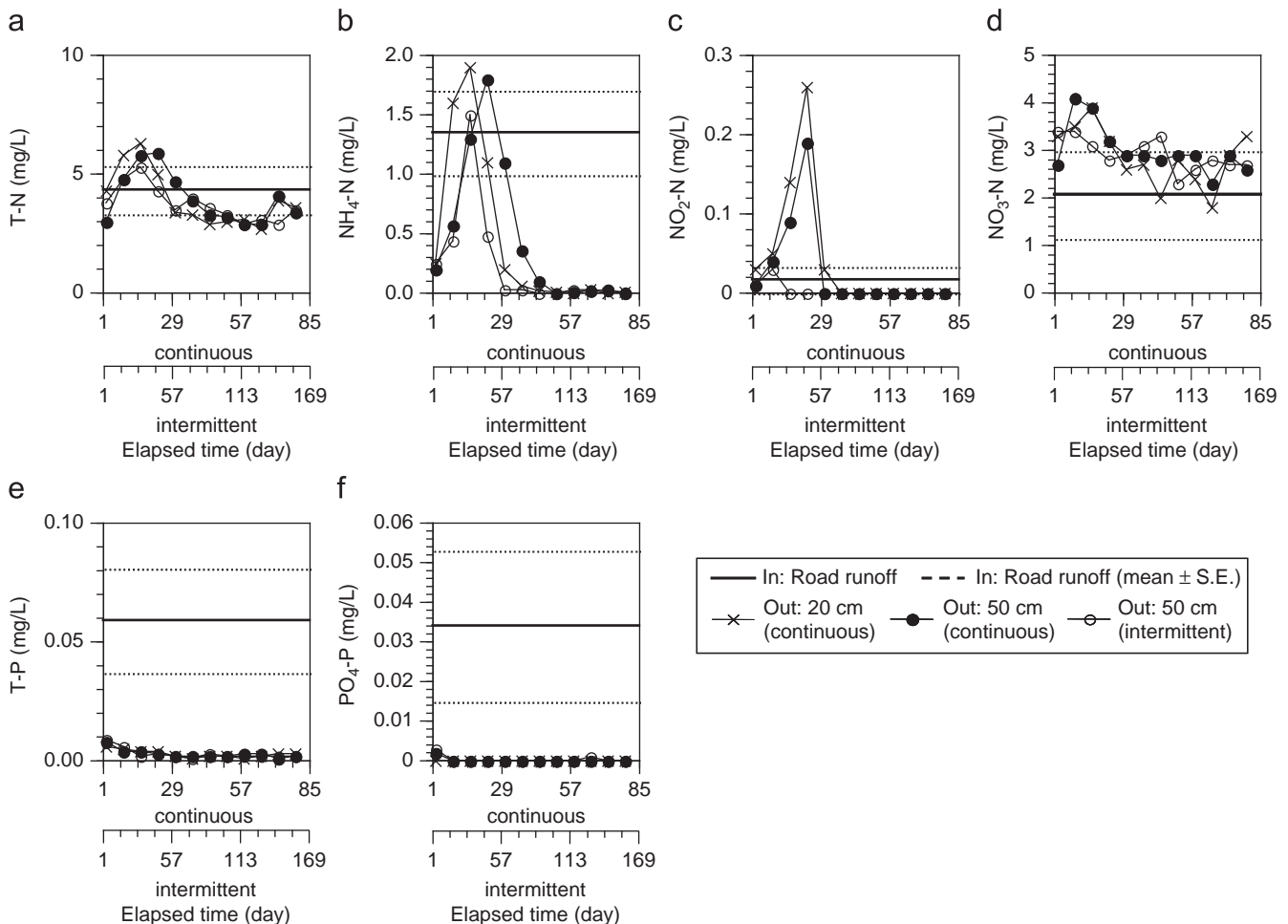

Fig. 3 – Behaviour of (a) T-N, (b) NH_4-N, (c) NO_2-N, (d) NO_3-N (e) T-P and (f) PO_4-P in the artificial road runoff water and infiltrated water.

3.4. Metals

Fig. 4(a–d) shows the behaviour of Mn, Ni, Cu and Sr, as examples of metals. The behaviour of other metals is shown in Fig. S3. Paired *t*-tests showed that no significant differences were observed in behaviour between continuous and intermittent conditions for most of the metals ($P > 0.05$). Except for Mn, Ni and some alkaline earth metals (Mg, Sr and Ba), most of the other metals (Be, Al, Cr, Fe, Co, Cu, Zn, As, Mo, Sb, Pb and V) were considerably removed by the soils (overall removal efficiencies: 57–100% for the 20-cm column (continuous), 71–100% for the 50-cm column (continuous) and 69–100% for the 50-cm column (intermittent)). The efficient removal of metals by the soils was consistent with previous findings that heavy metals accumulate on the surface sediments/soils within or below infiltration facilities (Mikkelsen et al., 1996; Dechesne et al., 2004; Murakami et al., 2007). In our previous study, a breakthrough of Cu was observed in the soil infiltration test using treated wastewater (Nakada et al., 2007). Interestingly, in the present study, Cu was efficiently removed by the soil infiltration treatment using the road runoff throughout the test (overall removal efficiencies for 3 columns: 99–100%), although the concentration of Cu in the road runoff water was 6 times higher than that in the treated wastewater in the previous study. This highlighted the possible contributions of other water quality parameters that govern the behaviour of Cu. The breakthrough of Cu in the test using treated wastewater and its significant removal in the test using road runoff water can be explained by the difference in the aqueous speciation of Cu or the characteristics of organic matter newly adsorbed onto the soils during the test. Copper is likely to be associated with organic matter in both aqueous and solid phases (Banerjee, 2003; Murakami et al., 2008). The differences in the speciation of Cu between the 2 types of water might result in different mobility through the soils. Conceivably, the organic matter adsorbed from the road runoff water onto the soils could provide new adsorbed sites for Cu.

On the other hand, a clear breakthrough of some alkaline earth metals (Mg, Sr and Ba) was observed. The removal efficiencies decreased with an increase in the fed volume, particularly in the 20-cm column that has less sorption capacity. Nickel was also detected in the infiltrated water in the late stage (44–79 days under the continuous condition and 87–157 days under the intermittent condition). This finding is consistent with the previous report that Ni is the one of the potential groundwater pollutants from stormwater infiltration practices (Pitt et al., 1999). Paired *t*-tests showed that Ni was significantly removed under the intermittent condition than under the continuous condition in the late stage ($P < 0.05$). The major accumulative phases of Ni were organic matter as well as residual fractions (Stone and Marsalek, 1996). As shown in Fig. 2, organic matter was adsorbed onto the soils more significantly under the intermittent conditions than under the continuous condition. The newly adsorbed organic matter onto the soil column might function to bind Ni. In the initial stage, the concentration of Mn in the infiltrated water was more than 5 times higher than that in the road runoff and decreased gradually with an increase in time. This shows that Mn was released from the soils in the initial stage. It is known that reducing environments promote the release of Fe oxide and Mn oxide and As (Takahashi et al., 2004). Since the release of Fe and As was not observed in this study, the release of Mn was not attributed to the reducing environments. To understand the mechanisms of the adsorption and desorption phenomena of heavy metals such as Cu and Mn, further studies should be carried out to determine the speciation in aqueous and solid phases.

3.5. PAHs

Fig. 5(a) shows the behaviour of total PAHs (sum of quantified 13 PAH species). In the initial stage, the concentration of PAHs in the infiltrated water was approximately 3 times higher
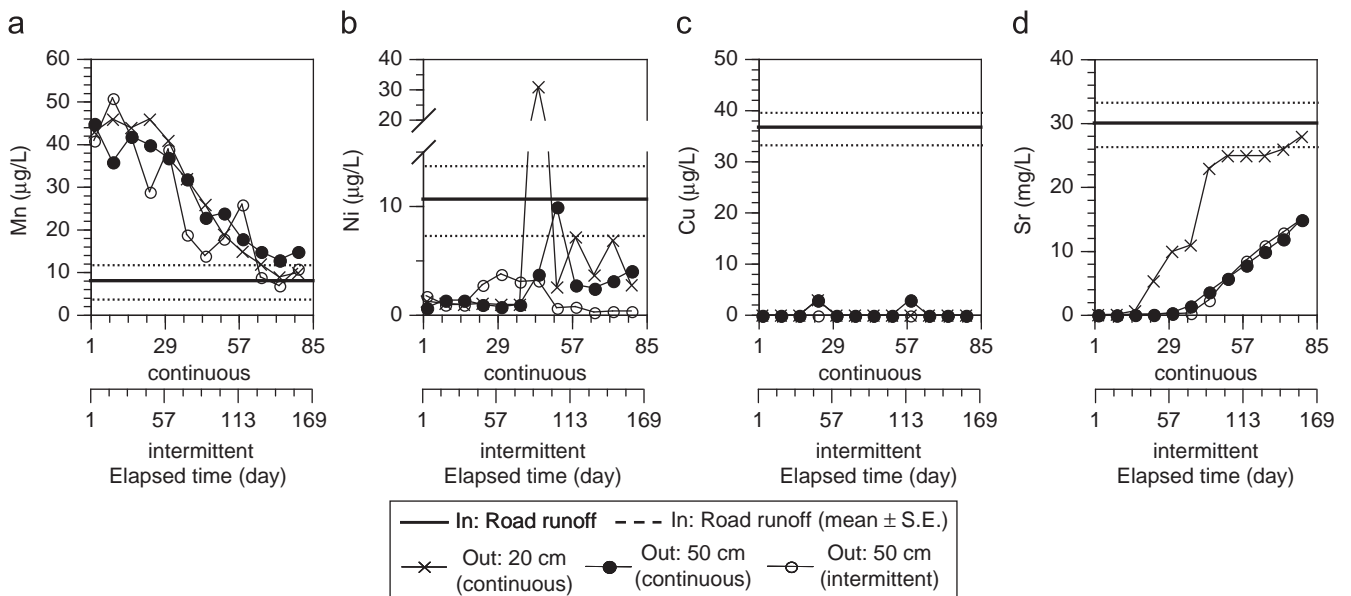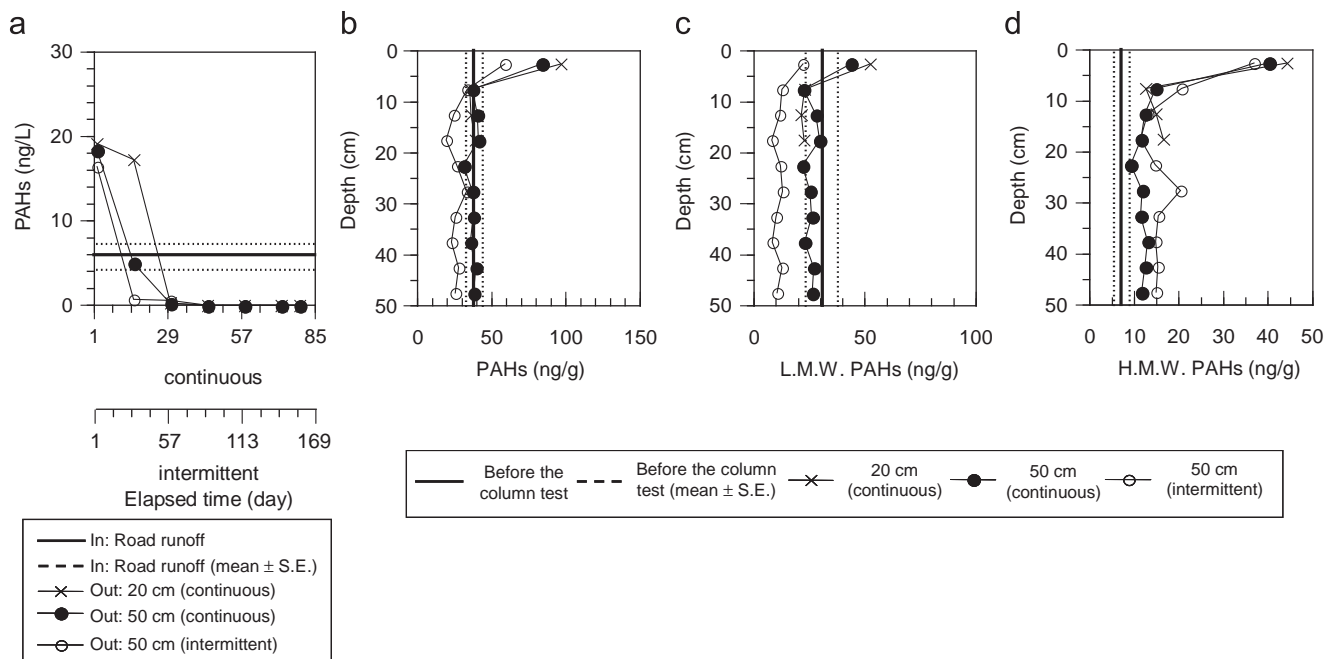

Fig. 4 – Behaviour of (a) Mn, (b) Ni, (c) Cu and (d) Sr in the artificial road runoff water and infiltrated water.

Fig. 5 – (a) Behaviour of PAHs in the artificial road runoff water and infiltrated water. (b–d) Depth distribution of PAHs in the soils. PAHs, total 13 PAHs; L.M.W. PAHs, 6 low-molecular-weight PAHs; H.M.W. PAHs, 7 high-molecular-weight PAHs.

than that in the road runoff water. This shows that PAHs were released from the soils. Striebel et al. (1994) observed a relationship between DOC and the dissolved phase of PAHs in road runoff and suggested that DOC acts as a solvent for PAHs. The release of PAHs from the soils was probably attributed to the surface-active compounds present in the artificial road runoff water. However, PAHs were not detected in any infiltrated water in the late stage and, eventually, PAHs were removed by soils (overall removal efficiencies: 17% for the 20-cm column (continuous), 56% for the 50-cm column (continuous) and 71% for the 50-cm column (intermittent)). This finding is also consistent with previous reports that PAHs were accumulated on the surface soils below the infiltration facilities (Mikkelsen et al., 1996; Dechesne et al., 2004). Fig. 5(b–d) shows the depth distribution of total PAHs, low-molecular-weight PAHs (fluorene–pyrene) and high-molecular-weight PAHs (benzo(a)anthrathene–benzo(g,h,i)perylene). The PAH content in the surface soils was clearly high. PAHs in road runoff are predominantly bound to particles (Kumata et al., 2000). Colloidal and fine particulate PAHs in the artificial road runoff should be trapped onto the surface soils because in this study, the artificial road runoff water contained colloids and fine particles. A significant difference was observed in the PAH content of the soils between continuous and intermittent conditions (paired t-test, $P < 0.05$). Except for the surface soils, the PAH content after the test under the continuous condition was almost comparable to that before the test; however, the PAH content decreased after the test under the intermittent condition. This decrease was particularly prominent in the case of low-molecular-weight PAHs. Low-molecular-weight PAHs are known to undergo biodegradation as well as evaporation (Bamford et al., 1999; Moretto et al., 2005). This result indicated that the intermittent

condition promoted the biodegradation and/or evaporation of low-molecular-weight PAHs.

3.6. PFOS and FOSA

Fig. 6(a and b) shows the behaviour of PFOS and FOSA that is one of the precursor compounds of PFOS. No significant differences were observed between continuous and intermittent conditions for PFOS and FOSA (paired t-test, $P > 0.05$ for both). PFOS was removed by the soils in the initial stage; this result was supported by the finding that the sorption of PFOS onto the solids was related to hydrophobic and electrostatic interactions (Higgins and Luthy, 2006). However, the PFOS concentration in the infiltrated water increased gradually. In particular, in the late stage, the concentration of PFOS in the infiltrated water that passed through the 20-cm column was higher than that in the road runoff water. In the parallel study, we found a significant relationship in removal efficiencies of water-soluble micropollutants between the soil infiltration treatment and wastewater treatment plants (Shinohara et al., 2006). The mass loading of PFOS was known to increase after wastewater treatment due to the production of PFOS from biodegradation of its precursors (Sinclair and Kannan, 2006). It was also considered that precursors contribute to the higher concentration of PFOS in the late stage. To our knowledge, this is the first report to suggest that PFOS is produced through biodegradation of the precursors during soil infiltration. FOSA was also not removed by the 20-cm column, although its breakthrough was slower than that of PFOS. These results indicated that PFSs could finally reach the groundwater. In particular, the increase in PFOS concentration is a matter of concern with regard to groundwater contamination.
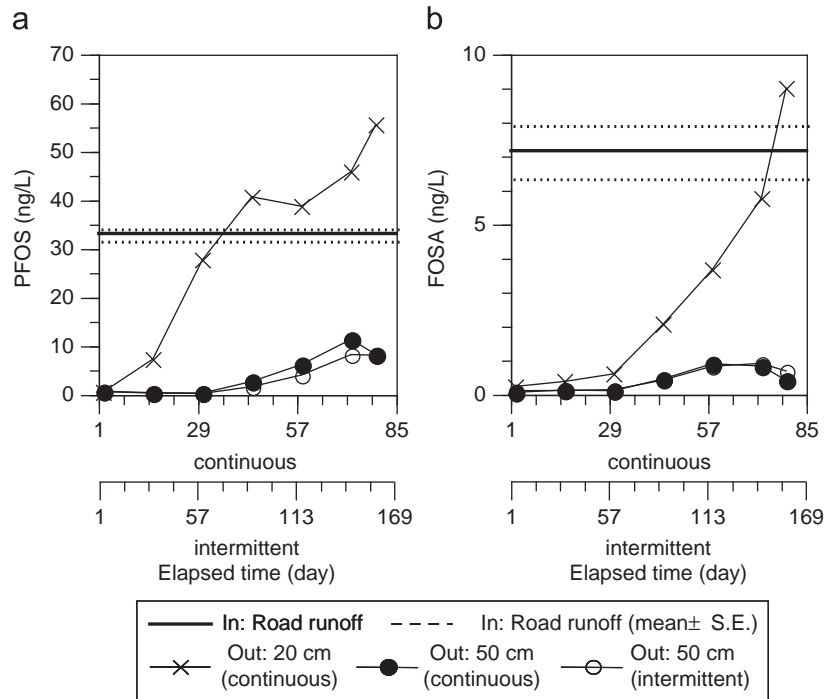
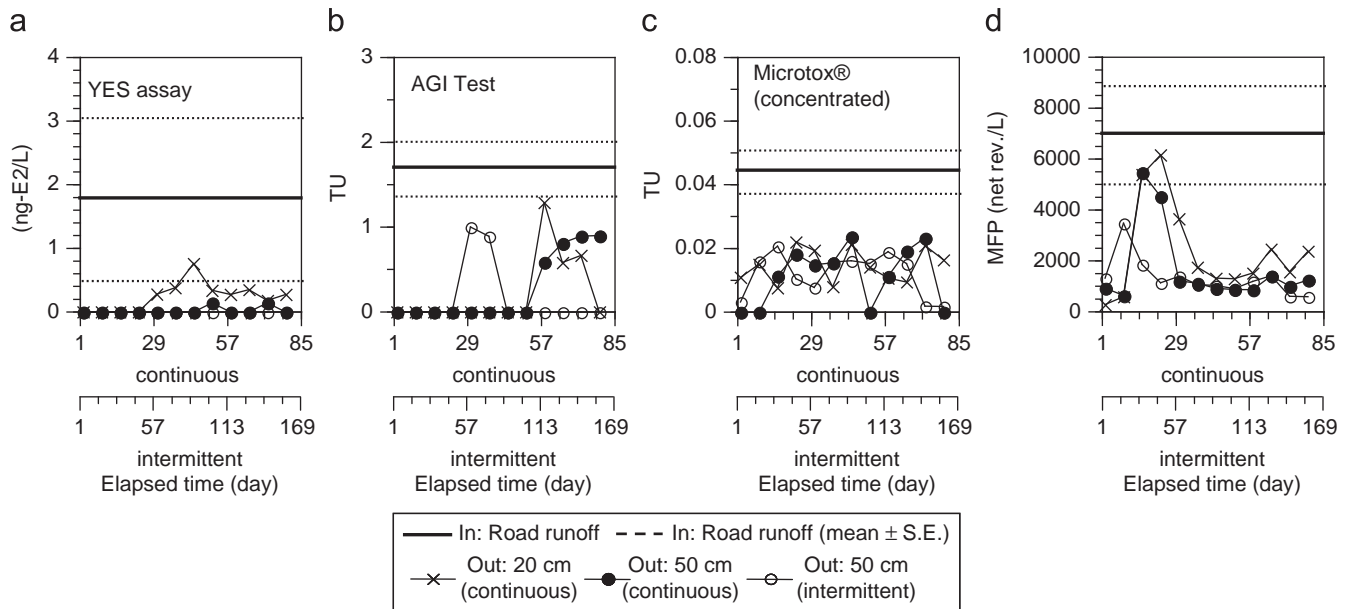Fig. 6 – Behaviour of (a) PFOS and (b) FOSA in the artificial road runoff water and infiltrated water.

Fig. 7 – Variation in toxicities in the artificial road runoff water and infiltrated water as determined by bioassay tests ((a) YES assay, (b) AGI test, (c) Microtox® (concentrated samples) and (d) MFP).

3.7. Bioassay tests

Fig. 7(a–d) shows the variation in toxicities as determined by the YES assay, AGI test, Microtox® and MFP. Toxicity unit (TU; $100/EC_{50}$) (USEPA, 1991) was used for measuring toxicity in the AGI test and Microtox®. In the YES assay, the removal efficiency of oestrogenic activities temporarily decreased in the 20-cm column in the period between 37 and 51 days;

however, sufficient removal was achieved in the late stage (cumulative late-stage removal efficiencies for 3 columns: 81–100%). One of possible explanations on this revival of removal efficiency was biodegradation along with significant increase in bioactivation. High removal efficiencies of oestrogenic activities by the soils were consistent with those observed in our previous study (Nakada et al., 2007). In the AGI test, the revival of removal efficiencies was also observed

in both the 20-cm column (continuous) and the 50-cm column (intermittent). The effective removal of toxicities observed in the AGI test in this study (removal efficiencies for 3 columns: overall, 85–90%; late stage, 68–100%) was in contrast to a high level of inhibition observed in the infiltrated water subjected to the soil infiltration treatment using treated wastewater (Nakada et al., 2007). As shown in Fig. S4, the Microtox® test using nonconcentrated samples revealed that toxicities in the infiltrated water were effectively removed by the soils in the late stage (cumulative late-stage removal efficiencies for 3 columns: 87–100%), despite a high level of toxicities in the initial stage. In the Microtox® test using concentrated samples, the removal efficiencies were constant throughout the test (removal efficiencies for 3 columns: overall, 67–72%; late stage, 67–73%). The concentrated samples reflect the effect of hydrophobic pollutants on bacteria, while the nonconcentrated samples reflect the effect of both hydrophobic and hydrophilic pollutants on bacteria. Therefore, the high level of toxicities in the infiltrated water in the initial stage was attributed to hydrophilic pollutants. The MFP test revealed that genotoxicity in the infiltrated water was relatively high in the initial stage and decreased in the late stage; this result was similar to that observed in the Microtox® test using nonconcentrated samples. High removal efficiencies of MFP were observed in the late stage, particularly in both 50-cm columns (cumulative late-stage removal efficiencies: 75% for the 20-cm column (continuous), 85% for the 50-cm column (continuous) and 86% for the 50-cm column (intermittent)). Overall, the bioassay tests revealed that toxicities were effectively removed by the soils. Table S1 shows a correlation matrix between the toxicities that were determined by bioassay tests and the chemical pollutant concentrations. The variations in toxicities observed in the AGI test and Microtox® were not strongly correlated with pollutant concentrations ($R^2 < 0.40$), indicating that multiple effects of several pollutants including unknown substances contributed to the toxicities. A relatively strong correlation was found between MFP and COD_{Mn} ($R^2 = 0.58$), likely because several mutagen precursors were organic matter. To identify pollutants that effect toxicities, further investigations including a toxicity identification evaluation (USEPA, 1991) are needed.

3.8. Recommendations

This study used multiple chemical analyses and bioassay tests to identify the pollutants in road runoff that possibly reach the groundwater. Limited amounts of NO_3, Mn, Ni, alkaline earth metals, PFOS and FOSA were removed by the soil, allowing these pollutants to reach the groundwater. These results indicate that infiltration facilities should be constructed at sites where road dust and runoff are minimally contaminated by these potential pollutants. Furthermore, controlling the sources of these pollutants as well as additional treatments before infiltration (e.g. plant uptake and adsorber systems) would be a prospective application to promote the reuse of road runoff. Infiltration facilities along with pollutant control will help to ensure a sustainable urban water cycle.

4. Conclusion

In this study, the removal efficiencies of pollutants in road runoff by soil infiltration were evaluated using multiple chemical analyses and bioassay tests. On the basis of this work the following conclusions are drawn:

- Organic matter (COD_{Mn} and DOC), T-P and PO_4-P were sufficiently removed by the soils throughout the test. NO_3, which was produced during nitrification by bioactivation, was not removed by the soils.
- Except for Ni, Mn and alkaline earth metals, most of the other metals such as Cu and Zn were effectively removed.
- PAHs were significantly removed in the late stage of the test. The intermittent condition facilitated the biodegradation and/or evaporation of low-molecular-weight PAHs.
- PFOS and FOSA were not removed by the 20-cm-deep soil column in the late stage. The soil infiltration treatment increased the concentration of PFOS, possibly due to the production of PFOS from biodegradation of its precursors.
- The YES assay indicated sufficient removal of oestrogenic activities. Other bioassay tests such as the MFP test also revealed that toxicities were effectively removed by the soils in the late stage.
- NO_3, Mn, Ni, alkaline earth metals, PFOS and FOSA possibly reach the groundwater and cause contamination.

Appendix A.   Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.watres.2008.02.004.

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