

Supporting information for

Groundwater pollution by perfluorinated surfactants in Tokyo

Michio Murakami,^{†,‡} Keisuke Kuroda,[§] Nobuyuki Sato,^{||} Tetsuo Fukushi,[§]

Satoshi Takizawa,[§] and Hideshige Takada^{*,†}

[†] Laboratory of Organic Geochemistry (LOG), Institute of Symbiotic Science and Technology,

Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183-8509, Japan

[‡] "Wisdom of Water" (Suntory), Corporate Sponsored Research Program, Organization for

Interdisciplinary Research Projects, The University of Tokyo, 7-3-1 Hongo, Bunkyo, Tokyo

113-8656, Japan

[§] Department of Urban Engineering, Graduate School of Engineering, The University of Tokyo,

7-3-1 Hongo, Bunkyo, Tokyo, 113-8656, Japan

^{||} IDEA Consultants Inc. 1334-5, Riemon, Ohigawa, Sida, Shizuoka, 421-0212, Japan

Table S1. Characteristics of groundwater.

Sample ID	Date	Type of groundwater	Depth (m)	pH	ORP (mV)	EC (mS/m)
GW-301	19-Sep-2006	Unconfined groundwater	20 ^a	6.95	219	132
GW-302	25-Sep-2006	Unconfined groundwater	20 ^a	7.00	78	93
GW-303	25-Sep-2006	Confined groundwater	30	7.36	91	566
GW-306	19-Sep-2006	Confined groundwater	30 ^a	7.46	286	871
GW-502	21-Sep-2006	Confined groundwater	33	9.33	190	48
GW-701	21-Sep-2006	Unconfined groundwater	15 ^a	8.20	388	34
GW-801	25-Sep-2006	Unconfined groundwater	10 ^a	7.12	146	72
GW-902	21-Sep-2006	Unconfined groundwater	10 ^a	6.75	400	32
GW-1101	25-Sep-2006	Unconfined groundwater	10 ^a	7.60	134	336
GW-1206	21-Sep-2006	Confined groundwater	30	6.80	404	49
GW-1304	19-Sep-2006	Unconfined groundwater	10 ^a	6.36	442	41
GW-1401	19-Sep-2006	Unconfined groundwater	20 ^a	6.64	459	29
GW-1601	4-Oct-2006	Unconfined groundwater	30	6.75	412	23
GW-1602	4-Oct-2006	Unconfined groundwater	30	6.36	410	23
GW-2401	26-Oct-2006	Unconfined groundwater (Riverbed water)	12	6.8	n.a. ^b	33
GW-2501	20-Nov-2006	Springwater	0	6.1	n.a. ^b	20

^a Estimated values.

^b Not available.

Table S2 Monitored ions for analytes of interest.

	Parent ion (<i>m/z</i>)	Product ion (<i>m/z</i>)
PFOS	499	80, 99
FOSA	498	78, 478
PFHpA	363	169, 319
PFOA	413	169, 369
PFNA	463	169, 219
PFDA	513	219, 269
PFUA	563	169, 269
PFDDA	613	169, 319
PFTDA	663	169, 319
¹³ C-PFOA	415	169, 370

Table S3. PFS concentrations in groundwater in Tokyo [ng/L].

	PFOS	FOSA	PFHpA	PFOA	PFNA	PFDA	PFUA	PFDDA	PFTDA
GW-301	3.5	0.44	5.5	20	0.67	<0.4	<0.1	<0.1	<0.1
GW-302	90	1.3	20	60	94	2.0	1.0	0.70	0.65
GW-303	0.72	<0.1	2.4	4.3	1.2	<0.1	0.39	0.18	<0.1
GW-306	0.45	<0.1	0.56	2.0	0.44	0.63	<0.1	0.40	<0.1
GW-502	6.3	0.49	2.4	9.6	0.74	0.58	0.93	<0.1	<0.3
GW-701	4.6	<0.1	1.2	5.1	0.78	0.38	0.1	<0.1	<0.1
GW-801	5.8	<0.1	10	18	3.9	2.0	0.61	0.47	<0.3
GW-902	0.28	<0.1	1.1	3.9	0.15	<0.2	<0.1	<0.1	<0.3
GW-1101	12	0.15	<0.1	21	9.0	11	0.78	2.1	0.64
GW-1206	19	<0.1	1.6	5.7	1.3	<0.2	<0.1	<0.1	<0.3
GW-1304	1.3	<0.1	<0.1	0.47	0.1	<0.4	<0.1	<0.1	<0.1
GW-1401	32	<0.1	0.84	7.0	1.0	<0.4	<0.1	<0.1	<0.1
GW-1601	8.2	0.20	1.5	6.9	16	<0.1	<0.1	<0.1	<0.1
GW-1602	54	0.18	4.6	9.9	4.7	<0.1	<0.1	<0.1	<0.1
GW-2401	133	<0.1	3.6	21	16	<0.1	<0.1	0.35	0.31
GW-2501	6.5	<0.1	2.5	11	6.0	<0.1	<0.1	<0.1	0.12

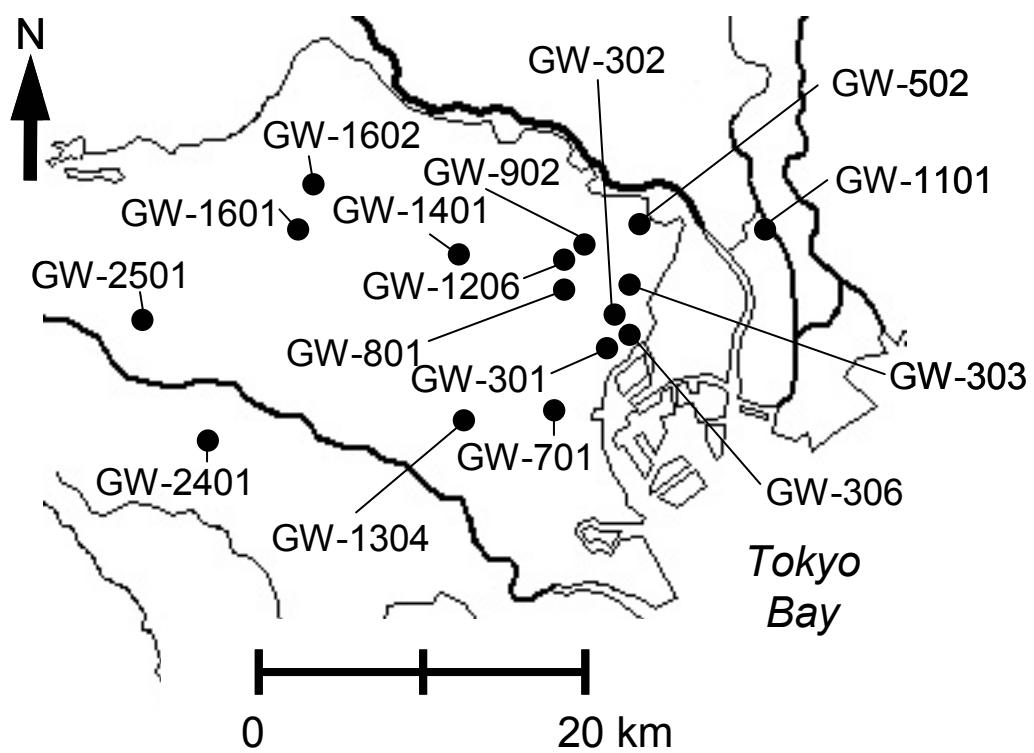


Figure S1. Sampling locations.

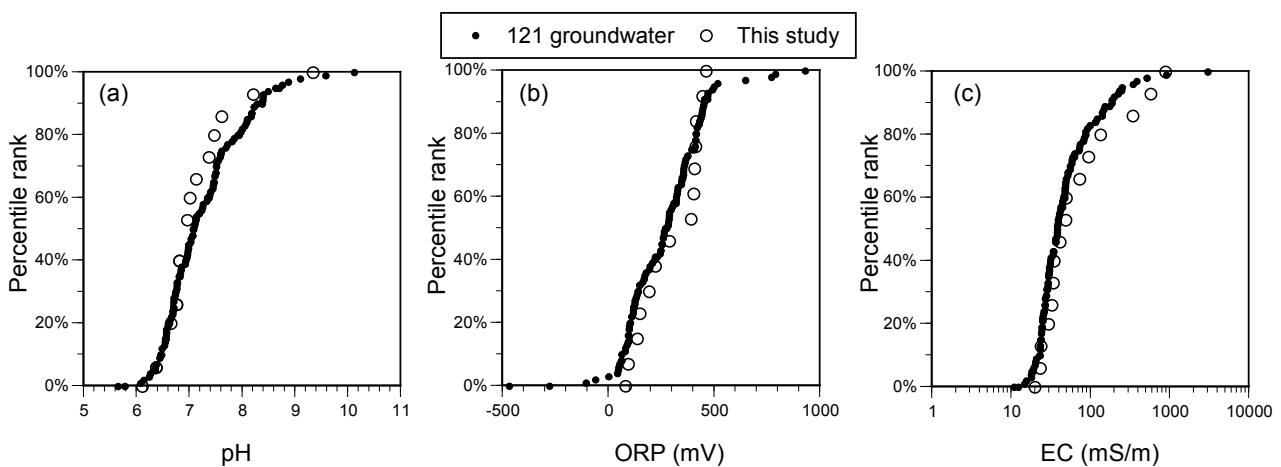


Figure S2. Comparison of distribution of pH, ORP, and EC between this study and 121 groundwater samples. (a) pH, (b) ORP, (c) EC.

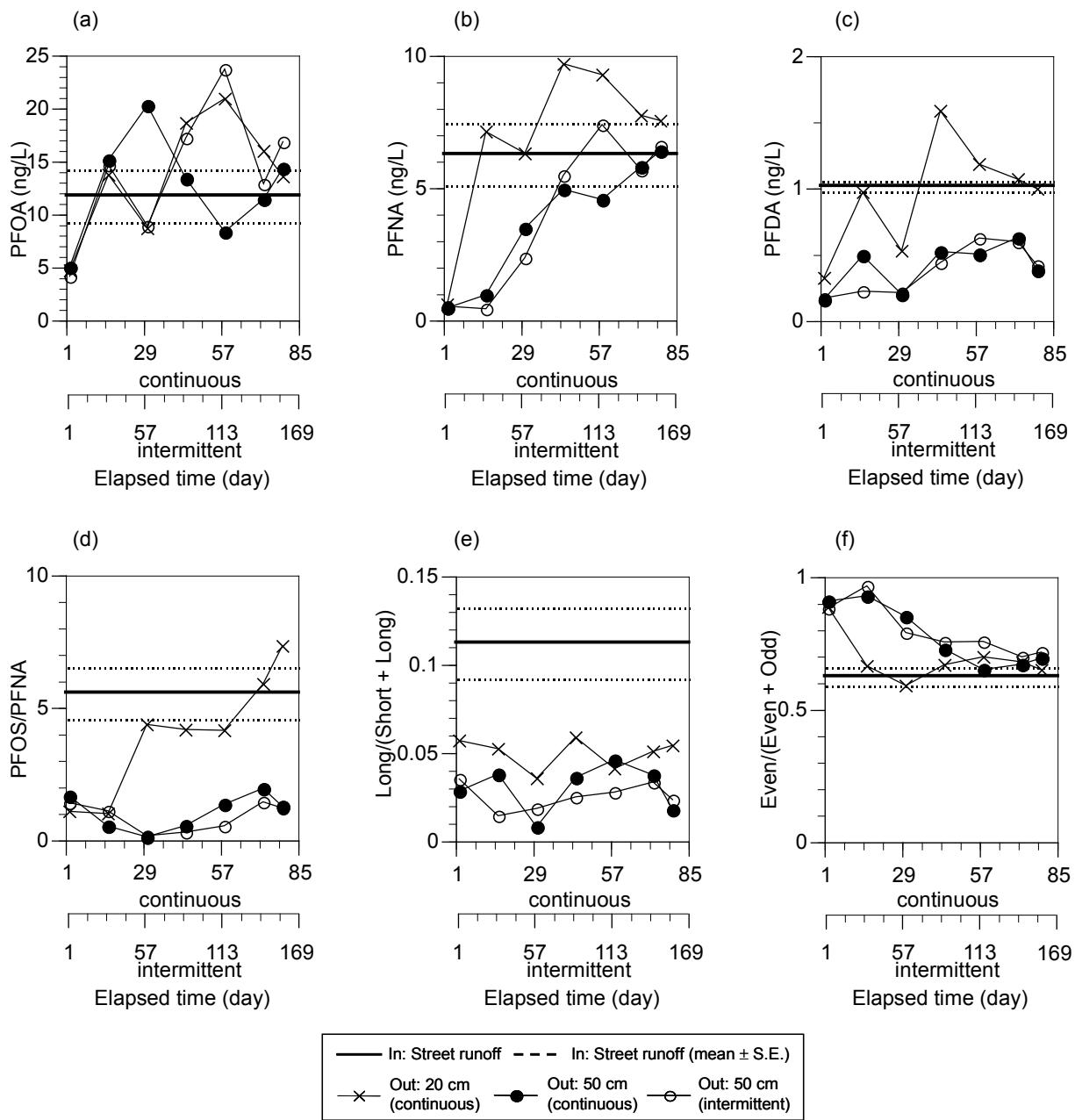


Figure S3. Variation in PFSS without the label-recovery correction in the artificial street runoff (influent) and infiltrated water (effluent). (a) PFOA, (b) PFNA, (c) PFDA, (d) PFOS/PFNA ratio, (e) Long/(Short + Long) ratio, (f) Even/(Even + Odd) ratio. (Short, PFOA + PFNA; Long, PFDA + PFUA; Even, PFOA + PFDA; Odd, PFNA + PFUA).

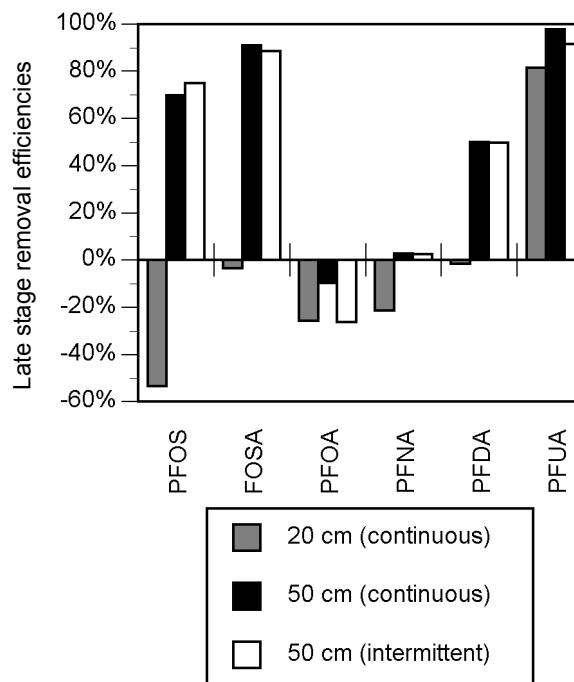


Figure S4. Efficiencies of removal of PFSs without the label-recovery correction in the late stage by soil (late stage, 72–79 days under continuous flow and 143–157 days under intermittent flow). Data of PFOS and FOSA come from ref (1).

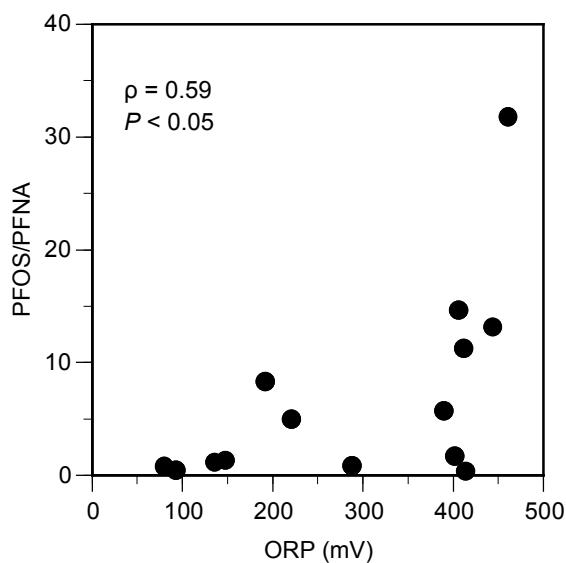


Figure S5. Relationship between ORP and PFOS/PFNA ratios in groundwater. Spearman's rank correlation coefficient (ρ) is shown in figures.

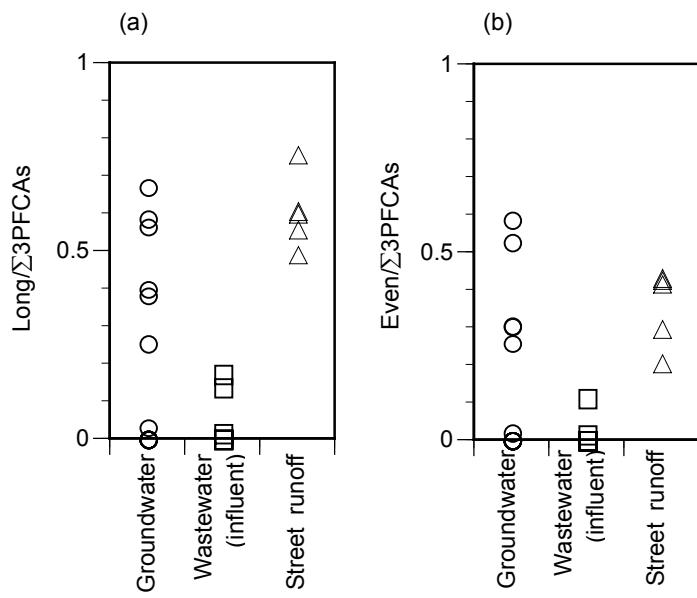


Figure S6. Comparison of Long/ $\sum 3\text{PFCA}$ ratios (a) and Even/ $\sum 3\text{PFCA}$ ratios (b) among groundwater, wastewater influents, and street runoff. Long/ $\sum 3\text{PFCA}$ ratios, $(\text{PFDA} + \text{PFUA})/(\text{PFNA} + \text{PFDA} + \text{PFUA})$; Even/ $\sum 3\text{PFCA}$ ratios, $\text{PFDA}/(\text{PFNA} + \text{PFDA} + \text{PFUA})$). Data of wastewater influents and street runoff were given by ref (2).

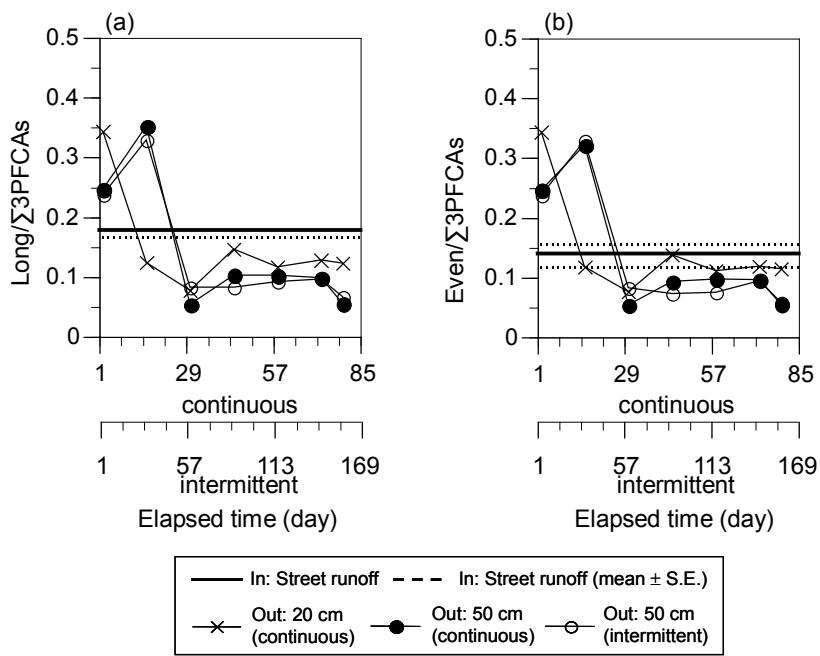


Figure S7. Variation of indicators in the artificial road runoff and infiltrated water. (a) Long/ Σ 3PFCA ratios ($(\text{PFDA} + \text{PFUA})/(\text{PFNA} + \text{PFDA} + \text{PFUA})$), (b) Even/ Σ 3PFCA ratios ($\text{PFDA}/(\text{PFNA} + \text{PFDA} + \text{PFUA})$).

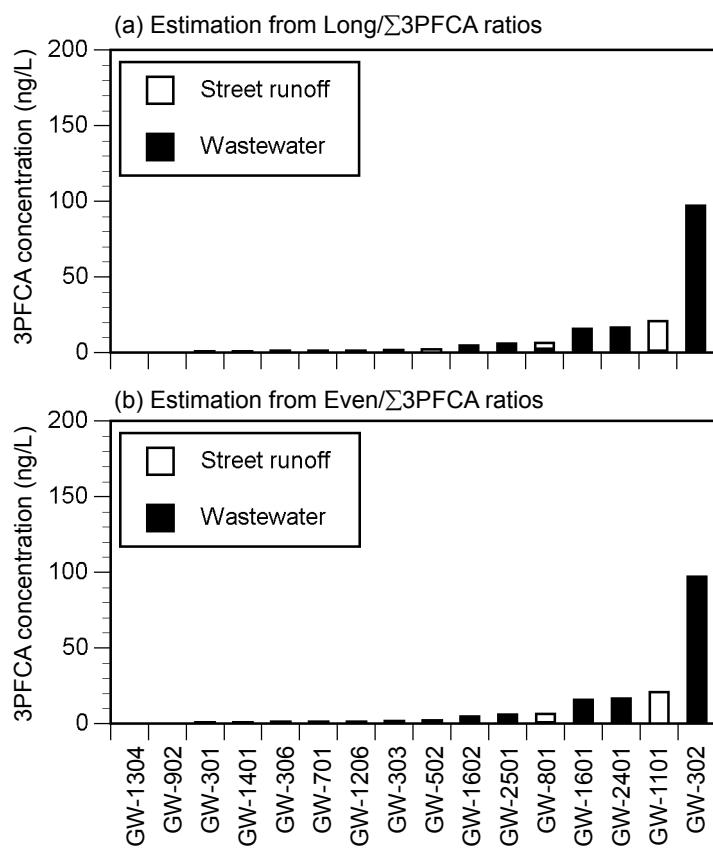


Figure S8. Contributions from wastewater and street runoff to 3 PFCAs in groundwater. (a) Estimation from Long/ \sum 3PFCA ratios ((PFDA + PFUA)/(PFNA + PFDA + PFUA)), (b) Estimation from Even/ \sum 3PFCA ratios (PFDA/(PFNA + PFDA + PFUA)).

Literature Cited

- (1) Murakami, M.; Sato, N.; Anegawa, A.; Nakada, N.; Harada, A.; Komatsu, T.; Takada, H.; Tanaka, H.; Ono, Y.; Furumai, H. Multiple evaluations of the removal of pollutants in road runoff by soil infiltration. *Water Res.* **2008**, *42*, 2745-2755.
- (2) Murakami, M.; Shinohara, H.; Takada, H. Evaluation of wastewater and street runoff as sources of perfluorinated surfactants (PFSs). *Chemosphere* **2009**, *74*, 487-493.