

FOOTPRINT OF FLUORINATED MIST SUPPRESSANT IN AMBIENT ENVIRONMENT CAUSED BY CHROME PLATING INDUSTRY

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Introduction

Using fluorocarbon surfactants as mist suppressant is an essential practice in electroplating industry, especially for hard chrome plating. In China, the most commonly used are based on perfluorooctane sulfonate acid and its salts (PFOS, $C_8F_{17}SO_3^-$), such as FC-80 ($C_8F_{17}O_3SK$, CAS No: 2795-39-3) and FC-248 ($C_{16}H_{20}F_{17}O_3NS$, CAS No: 56773-42-3). Besides, there's a China-specific mist suppressant, 6:2 chlorinated polyfluorinated ether sulfonate (6:2 Cl-PFAES) with the trade name F-53B^{1,2}. These poly- and perfluoroalkyl substances (PFASs) will be discharged after the expiration of the chrome plating bath. Due to their extreme stability, they have been detected in both the influent and the effluent of the dedicated wastewater treatment station as well as the vicinity river samples¹, and recently also in municipal sewage treatment plants². However, very few data about these PFASs in surrounding environment of chrome plating industry are available. In particular, ground water and biota samples have not been investigated previously.

The present study aims to investigate the footprint of fluorinated mist suppressant in surrounding environment caused by chrome plating industry. Nangezhuang Electroplating Plant (NEP), a typical middle-scale enterprise located in Daxing district of Beijing, China, was selected as the pilot facility. The chrome plating in NEP started in 1986 and has lasted for nearly thirty years.

Materials and methods

Chemicals

6:2 Cl-PFAES (F-53B) was obtained from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, with a purity of >98%. Potassium L-PFOS and ¹³C₄- and ¹³C₈-labeled L-PFOS, as recovery and injection standards (RS and IS), respectively, were purchased from Wellington Laboratories Inc. (ON, Canada). Solvents were HPLC grade (J.T. Baker, NJ), and ultrapure water was used (18 MΩ·cm, Millipore, MA).

Sampling

The map of sampling points is shown in Fig.1.

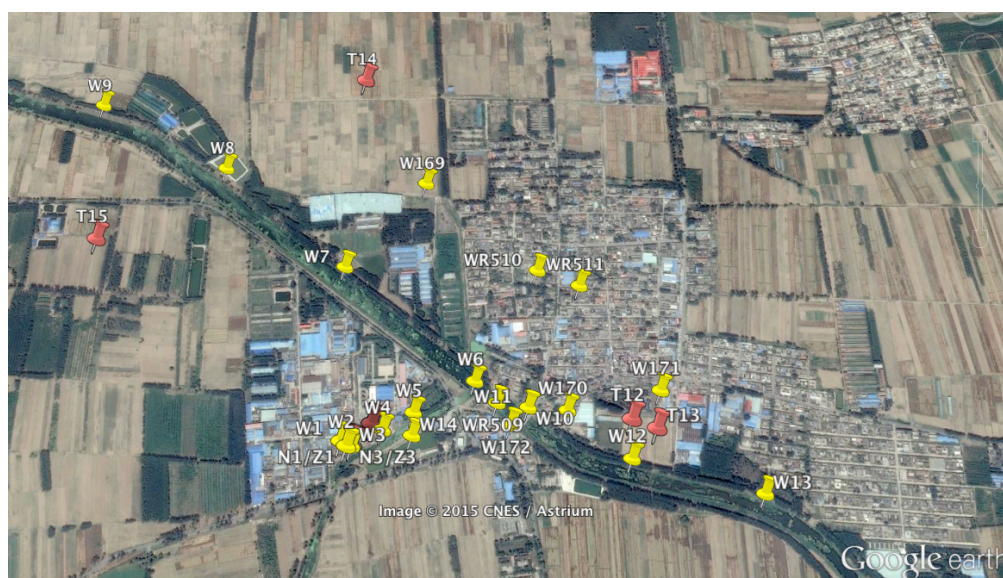


Fig.1 Map of sampling points (W-surface water; WR, N, Z-groundwater; T-Soil)

Two wastewater samples (W1, W2) were taken from two storage pools. Surface water samples were collected from the discharging ditch (W3-W5), the Tiantang River as the receiving water body (W6-W13), and a nearby fishpond (W14). Groundwater was sampled at 8 wells, including 3 registered monitoring wells (W169-171), 3 household wells (WR509-511), and 2 newly constructed monitoring wells (N1 and N3). Surface soil samples were collected from 15 points, including 7 in the sludge dumping site, 4 in the wastewater vaporization pool, and 4 in the nearby farmland. For N1 and N3, groundwater and soil at different depth was also sampled during their construction process. In addition, 4 carp samples of similar size (length=42-49cm, width=10-15cm, weight=0.99-1.44kg) were collected from the nearby fishpond which use the groundwater as the water source.

Sample preparation

All the water samples were collected in 500 mL polypropylene bottles with screw caps (Vitlab, Grossostheim, Germany) and filtered through glass microfiber filters (GF/F, 47 mm, Whatman, Kent, UK) before solid phase extraction (SPE). Oasis HLB cartridges (6 mL, 200 mg, Waters, MA) were first conditioned with 2×5mL methanol and then with 2×5 mL ultrapure water. Samples were introduced to the cartridges at a flow rate of 5–10 mL/min, dried and subsequently eluted with 2×5 mL methanol. The resulting extracts were reduced using a gentle stream of nitrogen, diluted to 1 mL with ultrapure water and filtered by a 0.22 μm nylon filter prior to analysis. The RS and IS were added at the amount of 25 ng for each sample before extraction and before instrumental analysis, respectively.

Soil samples were freeze-dried, homogenized and sieved through a 0.25mm stainless steel mesh to remove stones and other coarse materials. 0.5-2.0g samples were spiked with 25ng RS, extracted by 6mL of methanol, treated using ultrasonic at 30°C for 20min, then centrifuged at 3500rpm for 5min. The supernatant was collected in a precleaned 500mL PP bottle. These operations were repeated three times. In order to enrich the analyte and remove potential matrix interferences, the extracted solution was diluted with ultrapure water and loaded to SPE cartridges. PWAX cartridges (6mL, 150mg, Agela Technologies, China) were first conditioned with 4mL of ammonium hydroxide (0.5% NH₄OH in methanol), 4mL of methanol and 4mL of ultrapure water at a rate of 2 drops per second. Before loading the pH of extracted solution was adjust to pH=4 by using acetic acid solution. Samples were introduced to the cartridges at a flow rate of 5-10 mL/min. After loading the cartridge was washed with 4mL of 25mM sodium acetate and then dried with vacuum. Subsequently, the targets were eluted with 3mL of methanol and 3mL of ammonium hydroxide (0.5% NH₄OH in methanol). The resulting extracts were reduced using a gentle stream of nitrogen, diluted to 0.5 mL with ultrapure water and filtered by a 0.22 μm nylon filter prior to analysis. The IS were added at the amount of 25 ng for each sample before instrumental analysis.

The biological samples were homogenized by the use of ultra-turax. 0.5-1.0g of homogenized tissue was transferred to a 15 mL PP centrifuge tube and spiked with 25 ng RS, and 10 mL of acetonitrile was added to the tube for extraction. The following ultrasonic extraction, enrich and cleanup using SPE cartridges was all the same as soil sample pretreatment just mentioned above.

Instrumental analysis and QA/QC

Extractions were analyzed by high performance liquid chromatography-mass spectrometry (LC-MS/MS). Target compounds were separated on an ZORBAX Eclipse XDB C18 column (5μm×2.1mm×150 mm, Agilent, CA) using an UltiMate 3000 HPLC (Dionex by Thermo Fisher Scientific Inc., MA). Detection was achieved using an API 3200 triple quadrupole mass spectrometer (AB SCIEX, ON, Canada). The injection volume was 10μL for each sample. The column unit was held at 30 °C and the flow rate was 0.3 mL/min. Initial mobile phase condition was 40% methanol in 10mM ammonium acetate held for 1 min. A gradient ramp followed over 6min to 100% methanol, which was held for 3.5min, followed by equilibrium at 40% methanol for 2.5min. The mass spectrometer was operated in negative electrospray ionization mode with multiple reaction monitoring (MRM). The ionization was set at an ionspray voltage of -4.5 kV and at a temperature of 450°C, using nitrogen for drying. The flows of curtain gas, collision gas, ion source gas 1 and ion source gas 2 were set at 20, 5, 30, and 60 psi, respectively.

Sample concentrations were quantified based on an internal standard calibration curve. Field blank and procedural blank were checked without significant laboratory contamination or interferences. Duplicate samples and calibration check standards showed satisfactory reproducibility.

Results and discussion

PFASs in wastewater, surface water and groundwater

The detected concentrations of PFASs in water samples are shown in [Table 1](#).

Table 1 Detected PFASs in water samples

Sample point	Concentration (ng/L)								
	PFBA	PFHxA	PFOA	PFBS	PFPeS	PFHxS	PFHpS	PFOS	F-53B
<i>Wastewater</i>									
W1	ND	ND	4060	617	1360	4310	841	49600	45.1
W2	ND	ND	3720	ND	197	1020	172	29100	28.8
<i>Surface water</i>									
W3	2.52	1.35	13.5	1.26	3.22	13.1	2.98	86.6	0.86
W4	1.73	0.81	6.56	ND	1.67	6.52	1.45	47.2	0.41
W5	2.50	1.02	10.6	1.50	2.62	9.94	2.84	86.8	0.67
W6	2.68	1.18	13.0	1.41	2.26	8.00	2.22	85.2	0.73
W7	4.01	0.63	7.05	0.79	0.16	ND	ND	27.0	0.60
W8	4.50	0.78	7.86	0.71	0.11	ND	ND	18.4	0.34
W9	2.69	0.94	7.40	0.70	0.10	ND	0.01	24.1	0.54
W10	2.62	0.71	9.26	0.88	0.15	ND	0.15	31.6	0.57
W11	2.50	0.96	7.53	0.96	0.42	1.34	0.35	24.1	0.56
W12	2.56	0.68	8.48	1.02	0.34	0.86	0.33	51.4	0.87
W13	2.72	0.94	12.5	0.83	0.22	0.84	0.27	45.0	0.80
W14	2.98	0.69	8.98	0.80	0.10	ND	ND	42.2	0.57
<i>Groundwater</i>									
N1	13.0	13.6	21.2	2.34	ND	4.94	ND	113	17.0
N3	4.58	ND	8.50	1.26	ND	ND	ND	24.8	1.21
WR509	ND	ND	3.87	ND	ND	ND	ND	11.6	0.49
WR510	ND	ND	3.61	ND	ND	ND	ND	7.28	0.48
WR511	ND	ND	0.61	ND	ND	ND	ND	9.06	3.75
WR169	3.56	ND	10.1	ND	ND	1.07	ND	24.4	1.26
WR170	3.44	1.20	3.08	ND	ND	ND	ND	13.0	2.16
WR171	ND	ND	0.94	ND	ND	ND	ND	15.1	1.81

Fluorinated mist suppressants (PFOS and F-53B) as well as PFOA were found in all water samples, with the highest concentration in the wastewater from chrome plating. PFOA and other detected short chain perfluorinated sulfonate or acids might come from the impurity in the technical products, or the degradation of PFOS during the electroplating process. The rare detection of PFHxS and PFBS confirmed that these fluorocarbon surfactants have not been used as chrome mist suppressant in China.

The detected concentration of PFOS decreased from wastewater pool, discharging ditch to Tiantang River. Such trend should be caused by the dilution during the discharging process.

Both PFOS and F-53B were found in groundwater, with the detected concentrations much lower than those in surface water. The highest concentration was found in the well N1, which is very close to the wastewater discharging pool. The concentrations in WR509-511 were found to be lower, which is in consistent with the local flow direction of groundwater (i.e. from northwest to southeast).

PFASs in soil at the sludge dumping site

The detected PFASs in soil samples are mainly PFOS, as shown in [Table 2](#).

The highest concentration of PFOS was found at T3, i.e. 1174.05 ng/g. Like many other Chinese electroplating plants, the wastewater from NEP was treated by ferrous sulfate (FeSO₄) before discharging into the ditch

connected to the Tiantang River. During the treatment, large volume of sludge was generated. The separated sludge was then sent to the dumping site. The result from present study confirms the importance of sludge as the sink of PFOS. Nevertheless, the detected concentrations in soil samples from farmland nearby were much lower.

Table 2 Detected PFASs in soil samples (ng/g)

Sample point	PFOA	PFBS	PFHxS	PFOS	F53B
Dumping site					
T1	12.95	0.55	0.41	40.76	10.83
T2	12.14	0.55	0.22	51.47	10.45
T3	8.40	0.43	13.30	1174.05	7.46
T4	10.70	0.31	0.43	ND	4.00
T5	106.05	1.57	0.89	71.50	54.22
T6	11.70	0.34	0.49	25.89	ND
T7	21.98	ND	0.24	ND	5.66
Wastewater vaporization pool					
T8	31.78	1.51	0.45	82.03	20.57
T9	42.44	2.22	0.79	111.48	33.44
T10	36.13	1.46	0.33	98.56	22.80
T11	11.29	ND	0.47	47.17	ND
Farmland					
T12	10.73	0.31	0.11	21.65	4.78
T13	10.31	0.29	0.11	14.59	5.56
T14	9.32	0.17	0.12	20.16	4.55
T15	11.49	0.44	0.21	21.98	4.87

PFASs in fish

The detected PFASs in fish samples were mainly PFOS, with the concentration of 0.35-4.27ng/g (n=4, median=3.36 ng/g) in fish tissue, and 9.11-13.08 ng/g (n=4, median=11.17 ng/g) in fish liver. Such levels have not exceeded the criteria of 40 ng/kg according to the Reference Dose (RfD) of 0.077 µg/kg-day for calculating the allowable limit of PFOS in fish tissue, which was developed by the US Environmental Protection Agency (EPA)³.

In conclusion, the footprint of fluorinated chrome mist suppressant in surrounding environment of electroplating plant was investigated. PFOS is the main detected PFAS, with water as the important sink. Both surface water and groundwater should be of concerns. Sludge contains considerable concentration of PFAS, which highlights the necessity of including sludge in emission control. PFOS was also detected in edible fish in nearby pond, which should receive the concerns.

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