Assessing the Endosulfan Contamination in an Unconfined Aquifer

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Abstract Groundwater samples were analyzed in order to elucidate the fate of endosulfan in the soil and its release mechanism into water of an unconfined aquifer. Residual alfa endosulfan was determined in all the wells; however, beta endosulfan was below 0.001 μg/L. Maximum adsorption rates of alfa and beta endosulfan were 91%–86% on the topsoil; 87%–91% on the subsoil, respectively. About 13%–23% desorption rate on the topsoil and subsoil exhibited the probability of endosulfan movement in the soil. The study showed that a hydrophobic-moderately persistent pesticide can reach to groundwater despite the high clay content of soil.

Endosulfan (6, 7, 8, 9, 10-hexachloro-1, 5, 5a, 6, 9, 9a-hexahydro-6, 9-methano-2, 3, 4-benzodioxathiepin-3-oxide, CAS No. 115-29-7) is a chlorinated pesticide ($C_9H_6Cl_6O_3S$) of the cyclodiene group. Its technical preparation consists of alfa and beta isomers (70:30). World Health Organization (WHO) classifies endosulfan in Category II (moderately hazardous), while the US Environmental Protection Agency (EPA) lists it under the Category 1b (highly hazardous) pesticide (Tomlin 1998). Endosulfan contamination was monitored in the environment such as atmosphere, soils, sediments, surface and rainwaters and food staffs due to its abundant usage and stability. For example, it was detected at 0.2 mg/L level in the coastal lagoon of Dalyan, Turkey. It was found in at least 143 out of 1,416 National Priorities List sites by EPA and detected at levels of 0.2–0.8 mg/L in groundwater, surface water, rain, snow, and sediment samples. Higher concentration of endosulfan was found in surface water near the application areas.

Endosulfan is used extensively, throughout the world, as a broad spectrum insecticide on cotton crops, field crops such as paddy, sorghum, oil seeds and pulses, as well as vegetables and fruit crops (Goebel et al. 1982). The major crops grown in the area (Harran Plain) are cotton, wheat, corn and pulse. Especially cotton which requires extensive use of endosulfan is the main crop in the large irrigated plains (Atasoy et al. 2009). The Şanlıurfa Agriculture Directorate (The Plant Protection Branch Office) informed the endosulfan consumption in the Harran Plain as 9,634 L in liquid form and 73,850 kg in solid form in the year of 2009. The mean of endosulfan consumption for 5 years (between 2001 and 2006) was on the top level in the pesticide list (Atasoy 2007; Atasoy and Yesilnacar 2010). The increasing cotton farming in the plain caused the extensive use of endosulfan.

The risk of groundwater contamination by pesticides is ultimately determined by the relative rates of percolation, sorption, and degradation within the soil profile (Farran and Chentouf 2000; Masutti and Mermut 2007). As endosulfan is found in ground waters, it is apparent that there is a significant mobility of these chemicals through the soil system (Kumar and Philip 2006). Weakly adsorbed compounds are able to contaminate groundwater, as pesticide adsorption on soil retards the contaminant of water. However, Claver et al. (2006) suggested that endosulfan

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remains strongly adsorbed on the soil colloidal particles and it is considered safe for the groundwater.

The Harran Plain is located in the Şanlıurfa-Harran Irrigation District (Fig. 1). The Plain, which is 30 km wide and 50 km long occurring in the Southeast region of Turkey, between latitudes 36°43′–37°10′ North and longitudes 38°47′–39°10′ East (Fig. 2). Information about groundwater quality and groundwater management in the plain studied can be found in Yesilnacar and Gulluoglu (2007, 2008) and in Yesilnacar and Yenigun (2010). Because of the extensive agricultural use, it is thought that endosulfan will eventually reach the groundwater in the Harran plain and making it unsuitable as a drinking water. The objectives of this study were to: (i) determine whether the residual endosulfan exists in the groundwater (ii) understand the adsorption–desorption tendency of endosulfan in the soil, and (iii) find out factors such as soil, pesticide, and regional characteristics which contribute groundwater contamination, in case the residual endosulfan is found in the waters of the unconfined aquifer in the Harran plain, Southeastern Turkey.
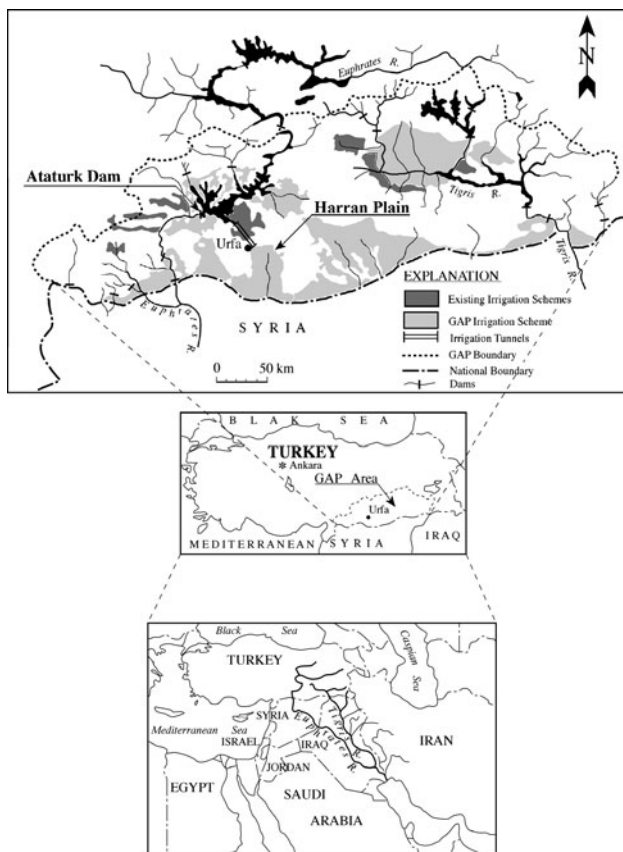

Fig. 1 Location map of the area studied

Materials and Methods

Groundwater samples were collected from 7 wells (sampling wells named after the village as Kızıldoruç, Yardımlı, Yaygılı, Cepkenli, Altılı, Bolatlar, and Uğraklı) in the Harran plain (Fig. 2) during the period of June and July 2006 (heavy irrigation period). The selected 7 wells are chosen among many that exist in the Harran Plain to make sure of their fair geographic representation of the groundwater in the plain. Average depth of sampling (for groundwater level) from ground surface was between 20 and 22 m during the period of June and July. Groundwater samples were brought to the laboratory and stored in the dark at temperature about 4°C prior to analyses within 24 h.

A soil profile was excavated and topsoil (0–27 cm) and subsoil (40–55 cm) samples-were taken for sorption studies. Adsorption–desorption tests were applied on the samples from topsoil (0–27 cm, Ap) and subsoil (40–55 cm, Bw2) to establish the fate of endosulfan in the solum. The topsoil (Ap) is the horizon that receives the endosulfan and subsoil (Bw2) is an intermediate transitional zone between the subsoil horizons and groundwater. Soil samples were air-dried, passed through a 2-mm sieve and stored in the closed-caps in refrigerator before their tests.

Adsorption–desorption tests were applied by using the batch equilibration method (OECD 2000) with a solid-to-liquid ratio of 1:5 for endosulfan adsorption–desorption studies. A preliminary kinetic experiment established the equilibration time for endosulfan adsorption–desorption. Equilibrium studies were conducted for duplicate samples of soil which initially conditioned with 0.01 M CaCl$_2$ solution for 16 h. Soil samples (5 g) were shaken with 25 mL of endosulfan solutions in 0.01 M CaCl$_2$ with initial concentrations of 0.020, 0.050, 0.080, 0,120, and 0.144 µg mL^{-1} for alfa endosulfan; 0.010, 0.025, 0.040, 0.060, and 0.075 µg mL^{-1} for beta endosulfan. All the experiments included controls-with only endosulfan in 0.01 M CaCl$_2$ (no soil) and blanks-with the same amount of soil in 0.01 M CaCl$_2$ (without endosulfan). In the equilibrium studies, soils were treated with alfa endosulfan were shaken 3 h for both topsoil and subsoil. For beta endosulfan samples were shaken with 105 rpm, 3 h for topsoil and 6 h for subsoil, at 25 ± 1°C in the dark and then centrifuged at 3,100 rpm for 15 min. Alfa and beta endosulfan were extracted from the aqueous supernatant, analyzed, and all the reported results constitute the mean of duplicate measurements.

Desorption experiments followed the same experimental conditions and procedures used for the adsorption studies. After completion of the adsorption study, the entire reaction mixture was centrifuged and the supernatant was decanted carefully and analyzed for the residual endosulfan

Fig. 2 Study area showing location of the sampling wells
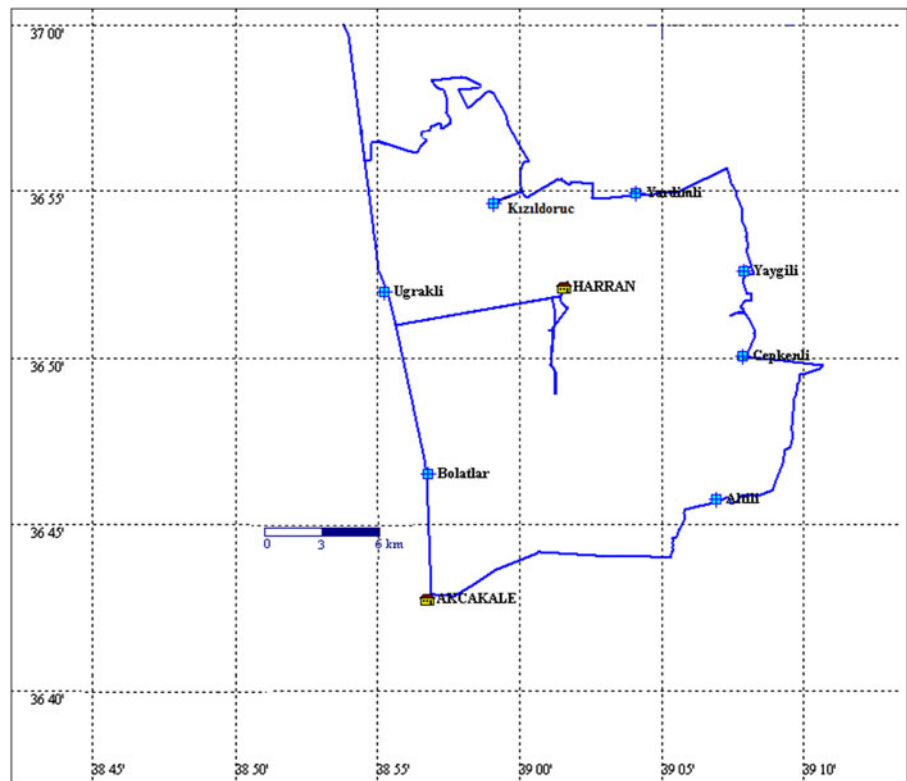
concentration. The same amount of decanted supernatant was replaced with 25 mL of endosulfan-free 0.01 M $CaCl_2$ solution. The suspensions were agitated for 1-2-3-6-10-24 h for both soils in the preliminary kinetic experiment to attain the desorption equilibria. In the equilibrium studies, alfa endosulfan was shaken for 4 h while beta endosulfan for 6 h for both soils. Desorption experiments were carried out as described above.

Alfa and beta endosulfan extraction processes were conducted on both the groundwater samples and the adsorption-desorptin test solutions. Alfa and beta endosulfan were extracted from samples using solid phase extraction (SPE) and EPA method 3535A (US EPA 1992). SPE cartridges and the processing unit (a disc holder consists of a conical flask and a glass top) were used in the extraction process. Solid phase extraction cartridges (Varian SPEC 47 $C_{18}AR$ Cat. No. A74819) were preconditioned with 5 mL of methanol, followed by 5 mL of deiyonized water, before the samples were loaded. Elution of endosulfan was obtained with 5 mL of acetone. The eluate was evaporated to dryness under a gentle stream of nitrogen gas, and the residue taken up in acetone prior to injection into the gas chromatograph (GC) for analyses. Exactly 1 L sample was concentrated to 5 mL of eluate in the SPE cartridge for the endosulfan extraction from the groundwaters used in this study. In this way the recovery percentages of both isomers were enhanced (200 times),

especially at low level concentrations. Therefore, the residual endosulfan could be attained at 0.001 ppb levels.

EPA method 8,081 was used for endosulfan analyzes (US EPA 1996). The extracts were analyzed in HP 6,890 Series GC with an electron capture detector (ECD) equipped with autosampler and with HP 19091 J-413 max 325°C, HP-S 5% phenyl methyl siloxane capillary column (30 m × 320 μm × 0.25 μm). The operating conditions were as follows: The injector temperature was set at 275°C and the detector temperature was 300°C. The oven was programmed to increase from 200 to 240°C at a rate of 3°C min^{-1} and to 290°C (hold for 1.17 min) at a rate of 10°C min^{-1}. Nitrogen (N_2) was used as the carrier gas at a flow rate of 80 mL min^{-1}. Retention time for alfa and beta endosulfan was 7.14 and 8.90 min, respectively.

Results and Discussion

Analysis results of alfa and beta endosulfan residues in seven wells are shown in Table 1. Residual alfa endosulfan was determined in all the wells; however, beta endosulfan was generally below the detection limit (0.001 μg/L). Alfa endosulfan concentrations in the groundwater were higher than that of beta endosulfan. This was due to the higher proportion of alfa isomer than beta isomer (70:30) in the content of technical endosulfan used extensively in Turkey,

including the Harran plain. Therefore, the amount of residual alfa endosulfan in the environment was expected to exceed the beta endosulfan. Nevertheless, all the samples that were analysed were below the maximum admissible concentration (MAC) of Standard 266 of the Turkish Standards Institution (TSE) regarding the quality of water intended for human consumption (Table 2) (TSE 2005).

Residual alfa endosulfan in the wells (except for Kızıldoruç well) increased a little in July 2006. This is due to the continuing irrigation on the cotton farms and the rising groundwater levels in this period (Kendirli et al. 2005; Yesilnacar and Güllüoğlu 2007; Yesilnacar and Güllüoğlu 2008). In places, water in drainage canals filled with water and mixed up with irrigation water and this mixture is used as irrigation water. It is also possible that the water in the soil macro-pores contributed to the transport of endosulfan molecules through the soil profile and caused the contamination of groundwater. Both alfa and beta endosulfan

levels in Kızıldoruç well decreased in July. It is thought that the contaminants in Kızıldoruç location were carried towards the low-lying areas in the plain. Annual endosulfan consumption in the plain, between the year 2001 and 2009, was presented in Table 3. The continuous endosulfan application in farmlands is likely causing retardation of its degradation time and acceleration of its transport through the soil profile and leaching to groundwater. Thus, the long-term using of endosulfan in Harran Plain causes the endosulfan contamination in the wells in the area studied. Extensive use of this pesticide more than a decade for cotton plantation in the Harran plain, southeast of Turkey is great concern regarding the potential transport in the environment.

Sorption is one of the key processes affecting the fate of agrochemicals in the sediment–water–soil environments (Thorstensen et al. 2001). A complete understanding of the adsorption and desorption of endosulfan is needed for

Table 1 Residual endosulfan concentration in the groundwater samples from Harran plain

Well No	Wells	Altitude (m)	Groundwater level (m) (from the ground)	June 2006		July 2006	
				Alfa endosulfan ($\mu g\ L^{-1}$)	Beta endosulfan ($\mu g\ L^{-1}$)	Alfa endosulfan ($\mu g\ L^{-1}$)	Beta endosulfan ($\mu g\ L^{-1}$)
1	Kızıldoruç	374	2.28	0.0381	0.0015	0.0377	BDL*
2	Yardımlı	367	3.50	0.0371	BDL*	0.0390	BDL*
3	Yaygılı	388	3.00	0.0366	BDL*	0.0383	BDL*
4	Cepkenli	380	1.82	BDL*	BDL*	0.0391	0.0032
5	Altılı	372	3.37	0.0363	BDL*	0.0404	BDL*
6	Bolatlar	365	7.50	BDL*	BDL*	0.0373	BDL*
7	Uğraklı	369	1.00	BDL*	BDL*	0.0399	0.0016

* *BDL* Below Detection Limit (Detection limit was 0.001 µg/L)

Table 2 MAC of pesticide in the drinking water (TSE 2005)

Characteristics	Maximum level		Unit	Explanation
	Class 1[a] and Class 2/Type 1[b]	Class 2/Type 2[c]		
Pesticides	0.10	0.10	µg/L	The determined levels are considered, respectively for the each pesticide type
Total pesticide	0.50	0.50	µg/L	Total of all pesticide concentrations

[a] Class 1: Spring water

[b] Class 2/Type 1: Treated spring water

[c] Class 2/Type 2: Drinking and using water not including spring water

Table 3 Endosulfan consumption in Şanlıurfa (Harran Plain), between the year 2001 and 2009

	2001	2002	2003	2004	2005	2006	2007	2008	2009
Endosulfan (liquid) (L)	115,793	93,855	70,612	102,805	54,359	32,352	67,059	15,600	9,634
Endosulfan (powder) (kg)	40,058	40,290	34,845	3,975	64,073	43,552	5,425	74,681	73,850

Table 4 Adsorbed and desorbed amount of endosulfan on topsoil and subsoil from Harran plain

| Initial concentration (mg L^{-1})		Adsorbed (mg L^{-1})		Adsorption (%)		Desorbed (mg L^{-1})		Desorption (%)	
Alfa	Beta	Alfa	Beta	Alfa	Beta	Alfa	Beta	Alfa	Beta
Topsoil (0–27 cm)									
0.020	0.010	0.018	0.009	91	86	0.003	0.002	17	23
0.050	0.025	0.045	0.021	90	85	0.008	0.005	17	22
0.080	0.040	0.072	0.033	89	83	0.009	0.007	13	20
0.120	0.060	0.106	0.050	88	83	0.013	0.010	12	19
0.144	0.075	0.127	0.062	88	82	0.016	0.011	13	18
Subsoil (40–55 cm)									
0.020	0.010	0.017	0.091	86	91	0.003	0.002	19	19
0.050	0.025	0.042	0.023	84	90	0.008	0.004	18	18
0.080	0.040	0.067	0.036	84	89	0.011	0.006	16	16
0.120	0.060	0.010	0.053	83	88	0.016	0.008	16	15
0.144	0.075	0.119	0.066	83	88	0.018	0.010	15	15

better understanding mechanisms and the prediction of pesticide movement in soils and aquifers (Clausen et al. 2001). Finding the residual endosulfan in the groundwater is primarily related to the sorption mechanisms in the soil. Adsorption and desorption rates of endosulfan isomers are presented in Table 4. From the results it was clear that, endosulfan adsorbed highly on the clayey Harran soil. Adsorption rates of alfa endosulfan for different initial concentrations ranged between 88% and 91% on the topsoil and 83%–87% on the subsoil. Beta endosulfan adsorption rates were between 82% and 86% on the topsoil and 88%–91% on the subsoil. Alfa and beta endosulfan were highly adsorbed on the topsoil and subsoil. According to the Giles classification (Giles et al. 1960), endosulfan adsorption isotherm was type L for both horizons which is typical of an adsorbent with a high affinity for the adsorbate (Fig. 3). Hydrophobic nature of endosulfan caused to increase the attraction to the soil surfaces. (Atasoy et al. 2009). However, Atasoy (2007) indicated that high adsorption and medium desorption tendency of the Harran soils was attributed to poor physical bonding (as Van der Waals force) between endosulfan molecules and the soil colloidal particles. Pesticide added to topsoil is immediately adsorbed by the clay size soil particles. Movement of endosulfan to elsewhere is mainly due to physical processes, unless they are degraded. Most probable ways are excessive irrigation water moving horizontally at the surface and vertically through cracks, as the soils in the plain are prone forming cracks.

Sorption of pesticides by inorganic clay particles and organic matter may take place by one or more of the following interactions: Van der Waals forces, H bonding, dipole–dipole interaction, ion exchange, covalent bonding, protonation, ligand exchange, cation bridging, water
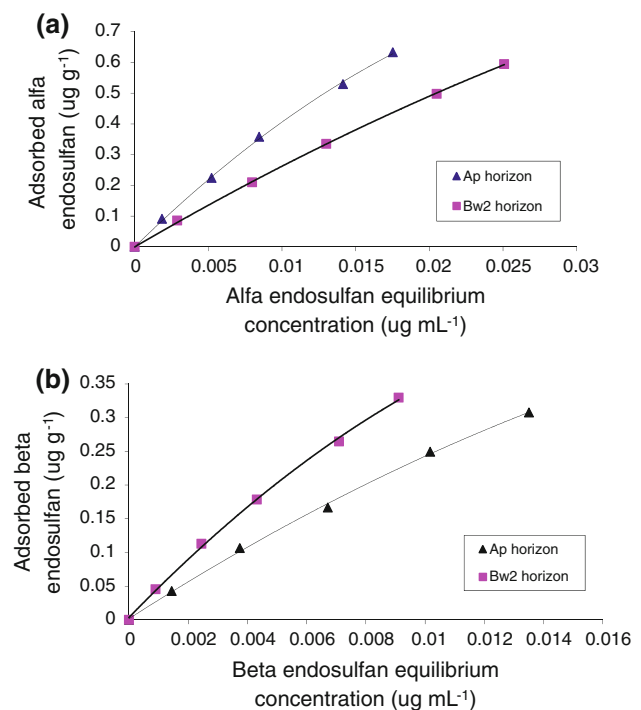
Fig. 3 Adsorption isotherms of (**a**) alfa and (**b**) beta endosulfan for the topsoil (Ap horizon) and subsoil (Bw2 horizon)

bridging, and/or hydrophobic partitioning. Sorption can also affect the persistence, biodegradability, leachability, and volatility of pesticides. Surrounding ecosystems can be impacted if conditions are conducive to pesticide drift, leaching, or surface runoff (Pierzynski et al. 1994). Loffredo et al. (1999) suggest that physical adsorption occurred between the nonpolar and/or hydrophobic pesticides and the soil. Atasoy et al. (2009) found that beta endosulfan desorption from the topsoil was higher than that of alfa

Fig. 4 Crack formations in the clayey Harran soils
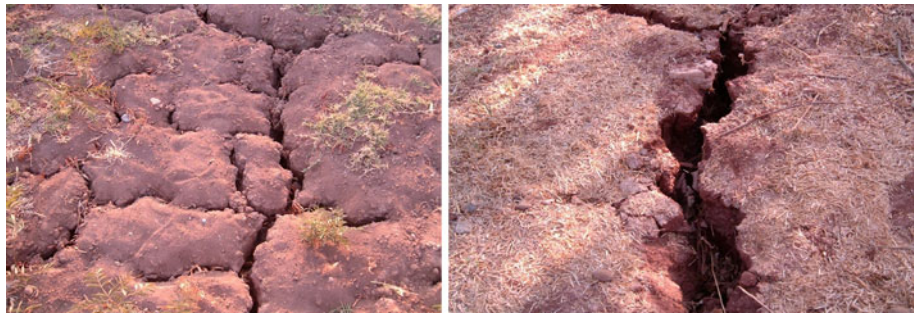
endosulfan and alfa and beta endosulfan desorption rates were about the same in the subsoil. About 13%–23% desorption rate (Table 4) on the topsoil and subsoil, respectively exhibited the probability of endosulfan movement in the soil. Thus, alfa and beta endosulfan moved down the profile and finally to the groundwater.

Vertisols are dominant in the Harran Plain (Dinç et al. 1995). These soils are characterized by a high content of swelling and shrinking type clays (>30%) to a depth of more than a m, which in dry seasons causes the soils to develop deep and wide cracks. A significant amount of material from the upper part of the profile may slough off into the cracks (Brady 1990). Deep cracks occurred in Vertisol in the Harran plain are shown on Fig. 4. Soil particles on the surface may go deep through these cracks, during even rainless period. Therefore, the adsorbed pollutants on the top soil may fall into these cracks, reaching the subsoil. Just as pollutants may drift horizontally to nontarget areas, they may also be moved vertically to subsoil by pedoturbation (Mermut et al. 1996; Atasoy 2008).

If the pesticide and metabolite degradation rates exceed their percolation rates through the soil, contamination of groundwater is less probable, but the occurrence of preferential flow increases the pesticide contamination risk. The study showed that a hydrophobic and a moderately persistent pesticide can reach to groundwater despite the high clay content of soil, thus alfa and beta endosulfan contaminated the groundwater in the irrigated Harran plain. The soil and pesticide characteristics, pedoturbation, extensive agricultural activities, excessive irrigation and incorrect or poor control on pesticide's use could all influence the groundwater contamination.

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