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Chemical Pollution and Transport of Organic Dyes in Water–Soil–Crop Systems of the Chinese Coast

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Many products including most daily necessities used by modern society are coloured using organic dyes to improve their aesthetic appeal, general attractiveness and acceptability for the end-use (Venkataraman, 1978; Webber, 1979; Delysse *et al.*, 1998). The insatiable demand by people has greatly stimulated the remarkable growth of the dye industry during the past 130 years (Litter and Chillingworth, 1974; Clonis *et al.*, 1987; Okada *et al.*, 1998). It has been estimated that at least two million different dye structures have been synthesized since the beginnings of the synthetic dye industry (Griffiths, 1984; Naskar *et al.*, 1998). In particular, it is found that there have been significant increases in the number of reactive dyes (Clonis *et al.*, 1987; Bae *et al.*, 1997; Juang *et al.*, 1997).

In China rural textiles and synthetic dye industries have developed rapidly in recent years (Zhou, 1995; Wu *et al.*, 1998). A large number of organic dyes have escaped and seeped into the environment due to backward dye-manufacturing and dye-producing technology. In addition wastewater, including domestic wastewater in particular and washing water containing various organic dyes have been directly discharged into the environment (Zhou *et al.*, 1996; Zhou and Wang, 1997; Zhou, 1999). Chemical pollution of organic dyes is noteworthy because the chemical toxicity and ecological harm caused by organic dyes is larger than other organic pollutants such as PAHs and PCBs (Zhou, 1995; Safarik *et al.*, 1997). Moreover, PAHs and PCBs that have been identified as carcinogens are two types of the degradation products from some organic dyes (Venkataraman, 1978; Zhou, 1995; Naskar *et al.*, 1998; Wu *et al.*, 1998; Low *et al.*, 1999).

Given these findings, what is the concentration of organic dyes polluting water and soil on the planet? What is the extent of organic dyes absorbed by plants from the soil? Do organic dyes move downward through soil into groundwater? At this time, few reports on these problems are available. The concentration, distribution and movement of organic dyes in water, crop and soil systems remain unclear.

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MATERIALS AND METHODS

Some suburbs of coastal cities with flourishing printing, dyeing and synthetic dye enterprises were selected as the objects of this investigation. These cities include Dalian, Tianjin, Qingdao, Suzhou, Shanghai, Ningbo, Shaoxing, and Guangzhou (Fig. 1). In consideration of the universality and representative of the sampling site, Jinan, Jinzhou, Xiamen, and Shantou were also selected.

At the first stage of this investigation surface water samples were systematically collected from streams, small rivers, lakes, ponds or wetlands that are close to or polluted by printing, dyeing and synthetic dye enterprises. At the same time surface soil samples (0-15 cm) were also collected in the cultivated lands with the invasion or irrigation of wastewater from printing, dyeing or synthetic dye enterprises.

At the second stage of this investigation the samples of subsurface soils at depths of more than 15 cm in the polluted sites were collected and analyzed in order to show the downward movement of organic dyes in soil profiles. Surface soils were also collected at 0, 0.5, 5.0, 20, 70 and 150 m from wastewater-discharging entrances in order to reveal horizontal movement of organic dyes due to the action of water flow and molecular dispersion of organic dyes.

Finally, crop samples including rice, wheat, potato, lotus root, radish, watermelon and soybean were selectively collected according to the analytical results of the surface soil samples. In other words, all the crop samples were collected from the cultivated lands with the pollution of organic dyes in order to verify the transport of organic dyes from agricultural soils to crops.

After round soil columns were built according to Figure 2, a solution containing 15.0 mg l^{-1} of reactive X-3B red dye was slowly sprayed on the top of soil columns. The total volume of the sprayed solution was 100 litre per treatment or soil column. The spraying lasted 2 weeks. Two days after the spraying was stopped, solutions leached into collectors were analyzed for reactive X-3B red dye. Soil samples at the depth of 20, 40, 60, 80 and 100 cm were collected and analyzed for reactive X-3B red dye.

After samples were collected fresh water, scraped soil and mashed plant samples were placed into triangular bottles with 100 ml of the organic extractant (petroleum aether : acetone = 1:1) and then shaken for 2.0 hr on a reciprocating shaker at 300 rev min^{-1} and at 25 °C. The water and organic phases of the shaken water sample mixtures were separated in separating

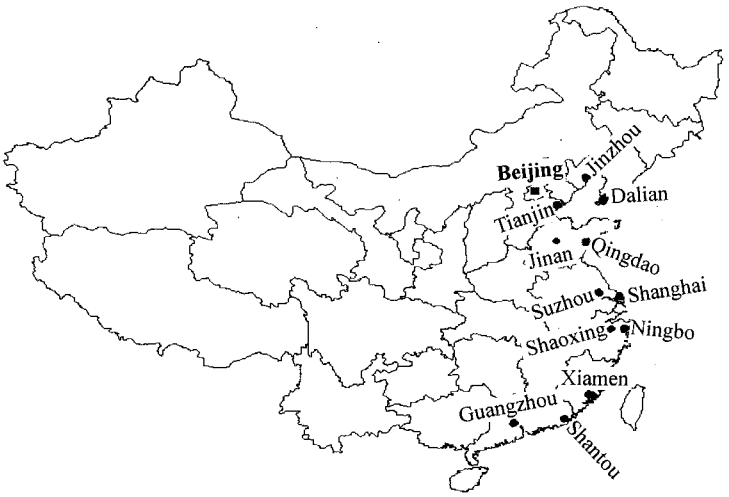

Figure 1. Sampling sites and possible dye-contaminated area coverage.

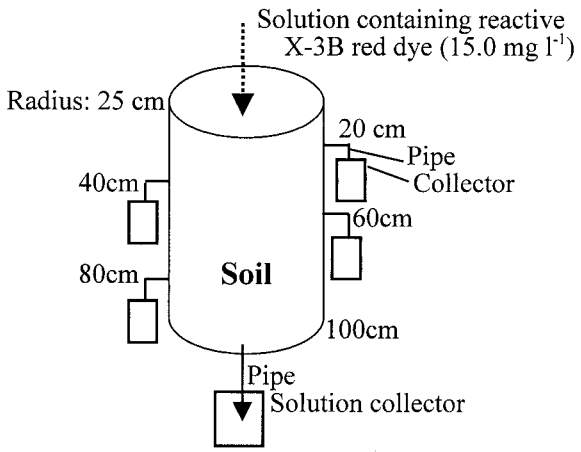

Figure 2. Soil column schematic.

funnels. The shaken suspensions from soil and plant samples were extracted for 0.5 hr on an ultrasonic generator (SB 2200 type, made in Shanghai) and centrifuged for 10 min at 6000 rev min^{-1} to separate the solid and solution phases. Acetone in the solution phases from soil and plant samples was washed and scoured off using distilled water. After the organic phases from water samples and the washed solutions from soil and plant samples were concentrated using anhydrous sodium sulfate, they were immediately analyzed using the gas chromatography (HP-6890 type) method (Ouyang *et al.*, 1986; Yang, 1993; Zhou, 2000).

Reactive X-3B red dye with the chemical structure in Figure 3 that was

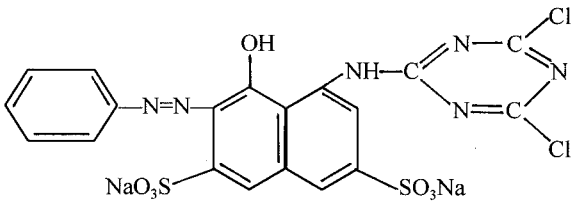

Figure 3. Chemical structure of reactive X-3B red dye

used as a reference chemical in the determination was provided from the Linan Chemical Plant, Zhejiang Province, China. The purity of this dye was 97.6%.

According to the history and current situation of production of organic dyes in coastal areas of China other organic dyes which were selected to be reference chemicals for the determination of organic dyes also included direct orange S, direct copper blue 2R, direct dark blue L, direct yellow brown D3G, direct black RN, direct light turquoise GL, acid violet 4BNS, basic green, basic brown, sulfur blue BN, disperse blue SE-2R, disperse golden yellow E-3RL, disperse orange S-4RL, disperse brilliant blue E-4R, reactive blue R-R, indigo, mordant black 2B, and leather coating black RL. The determination showed all the above-mentioned organic dyes had been detected in the sampling sites although there were different types of organic dyes in various sampling sites. In order to cover all the organic dyes occurring in the environment, particularly including organic dyes which were not detected in this study, experiential coefficient 1.1 multiplied by the addition of the concentrations of the above-mentioned organic dyes was regarded as the total concentration of organic dyes in water, soils and plants. Thus, the calculation formula can be expressed as follows:

$$\Sigma(\text{Organic dyes}) = 1.1\times(C_1 + C_2 + C_3 + \ldots + C_n) \quad (1)$$

Where Σ(Organic dyes) is total concentration of organic dyes (mg l^{-1} or mg kg^{-1}); C_1, C_2, C_3, ..., C_n represents the concentration of an organic dye detected in this study (mg l^{-1} or mg kg^{-1}).

RESULTS AND DISCUSSION

In most of the sampled ponds or wetlands near printing, dyeing or synthetic dye enterprises reactive X-3B red dye was detected (Table 1). However, the concentration of reactive X-3B red dye in water of the ponds or wetlands varied greatly, from 1.0 μg l^{-1} to 1232 μg l^{-1}. The average concentration of total organic dyes in the water of the ponds differed from the concentrations found in wetlands. The highest concentration of total organic dyes was found in the water of a wetland near a printing and dyeing enterprise in Guangzhou, up to 706 mg l^{-1}. In the water of East Lake, which is located at

Table 1. Organic dye concentration in ponds

Sampling site	Reactive X-3B red dye (μg l^{-1})		Σ(Organic dyes) (mg l^{-1})	
	Average	Range	Average	Range
Dalian: Near printing & dyeing plants	764 (n=60)	128-986	348 (n=60)	309-542
Tianjin:				
1) Near dye plants	43 (n=36)	6-123	169 (n=36)	123-198
2) Southeast suburb			48 (n=36)	6-74
Qingdao:				
Near dye plants			83 (n=60)	34-154
Suzhou:				
1) Near printing & dyeing plants	68 (n=60)	10-112	267 (n=60)	53-402
2) Developing area	453 (n=60)	245-603	399 (n=60)	203-446
Shanghai:				
1) Near Huangpu River	4 (n=60)	1-8	33 (n=60)	8-109
2) Western suburb	32 (n=60)	4-128	269 (n=60)	12-571
Shaoxing:				
1) Western suburb	687 (n=40)	401-892	78 (n=40)	68-83
2) Near dye plants	1009 (n=40)	925-1232	221 (n=40)	201-234
3) Keqiao Town	874 (n=40)	629-933	123 (n=40)	115-171
Ningbo:				
1) Near dye plants	412 (n=56)	213-523	109 (n=56)	87-123
2) Developing area	839 (n=56)	712-904	167 (n=56)	131-219
Xiamen: Near printing & dyeing plants			93 (n=60)	44-123
Guangzhou:				
1) Near printing & dyeing plants	123 (n=52)	44-218	332 (n=52)	269-706
2) Developing area			23 (n=52)	12-45

Shaoxing, reactive X-3B red dye was also detected, up to 15-41 μg l^{-1}. Undoubtedly, chemical pollution of organic dyes in most ponds, wetlands and lakes of this region was obvious.

In most of the sampled streams and small rivers organic dyes were not detected. Perhaps the difference in the occurrence of organic dyes between ponds/wetlands and small rivers/streams rests with following factors:
1) Ponds or wetlands are sensitive waters that are easily affected by the pollution sources of organic dyes;
2) Most organic dyes discharged into ponds or wetlands can be only detained and accumulated in the same ponds;
3) Organic dyes discharged into streams or small rivers may be diluted and taken away by running water;
4) The degradation of organic dyes in water may be very slow;
5) The dispersion of organic dyes in water is not slow.

Reactive X-3B red dye also existed in some agricultural soils of the eastern China (Table 2). In the surface soils near printing, dyeing or synthetic dye enterprises, the average concentration of total organic dyes was quite high,

Table 2. Organic dye concentration in surface soils

Sampling site	Reactive X-3B red dye (mg kg^{-1})		Σ(Organic dyes) (mg kg^{-1})	
	Average	Range	Average	Range
Dalian: Near printing & dyeing plants	0.71 (n=50)	0.02-1.3	433.9 (n=50)	134.4-1130.2
Jinzhou: Near printing & dyeing plants			76.3 (n=50)	18.0-321.5
Tianjin:				
1) Near dye plants	0.06 (n=50)	0.02-0.8	348.0 (n=50)	123.4-460.1
2) Southeast suburb			12.2 (n=50)	1.5-21.7
Jinan: Near dye plants			123.7 (n=50)	24.5-766.8
Qingdao: Near dye plants			204.8 (n=50)	8.7-1101.6
Suzhou:				
1) Near printing & dyeing plants	0.07 (n=50)	0.05-0.4	89.7 (n=50)	12.7-234.0
2) Developing area	0.23 (n=50)	0.01-0.6	45.3 (n=50)	23.3-102.9
Shanghai:				
1) Near Huangpu River	0.06 (n=50)	0.01-1.2	12.3 (n=50)	0.9-16.8
2) Western suburb	0.22 (n=50)	0.01-1.5	44.8 (n=50)	14.2-89.6
Shaoxing:				
1) Near dye plants	6.1 (n=50)	5.3-6.8	283.4 (n=50)	25.3-3114.0
2) Keqiao Town	2.6 (n=50)	1.8-3.4	92.5 (n=50)	62.3-133.1
Ningbo:				
1) Near dye plants	12.5 (n=50)	11.5-13.7	302.8 (n=50)	34.6-1235.6
2) Developing area	0.9 (n=50)	0.6-2.3	52.3 (n=50)	11.3-91.7
Xiamen: Near printing & dyeing plants			78.1 (n=50)	16.9-231.2
Shantou: Near printing & dyeing plants			76.8 (n=50)	18.9-198.0
Guangzhou:				
1) Near printing & dyeing plants	0.9 (n=50)	0.04-3.2	456.2 (n=50)	23.2-1238.1
2) Developing area			22.3 (n=50)	2.0-64.6

up to 12.3-456.2 mg kg^{-1} dry weight. The high concentration of organic dyes in surface soils mainly resulted from the long-term irrigation of wastewater containing organic dyes, namely, movement of organic dyes from surface waters to surface soils.

The concentration of total organic dyes in surface soils was inversely proportional to the distance from a wastewater entrance. The relationship could be expressed by following regression equation:

$$C = 1059.8\, e^{-0.0211d} \quad (n = 24, R^2 = 0.9435, \alpha<0.005) \quad (2)$$

Where C means the concentration (mg kg^{-1}) of total organic dyes in surface soils at 4 sampling sites, d is the mean distance (m) from a wastewater entrance. The relationship was also related to wastewater flux, the concentration of total organic dyes in wastewater, soil types and plants growing in the soils.

Table 3. Downward movement of organic dyes in soils affected by printing, dyeing or synthetic dye industries

Sampling site and soil type	Depth (cm)	Reactive X-3B red dye (mg kg^{-1})	Organic dyes (mg kg^{-1})
Jinzhou:			
Brown soil	0-15		321.5
(n=10)	15-35		49.7
	35-65		1.5
	65-100		Trace
Tianjin:			
Drab soil	0-15	0.8	460.1
(n=10)	15-35	0.01	52.1
	35-65	0.001	2.2
	65-85	No detected	Trace
Suzhou:			
Paddy soil	0-15	0.4	234.0
(n=6)	15-35	0.05	77.6
	35-65	0.003	12.4
	65-100	No detected	1.2
Shaoxing:			
1) Paddy soil	0-15	6.8	3114.0
(n=6)	15-35	1.4	261.5
	35-65	0.6	41.3
	65-100	trace	8.7
2) Red soil	0-15	5.3	25.3
(n=10)	15-35	0.8	8.1
	35-65	Trace	0.6
Ningbo:			
Paddy soil	0-15	13.7	1235.6
(n=6)	15-35	4.8	72.3
	35-65	0.9	11.2
	65-100	Trace	0.4
Xiamen:			
Paddy soil	0-15		159.5
(n=6)	15-35		23.1
	35-65		0.8
	65-100		trace
Guangzhou:			
Red soil	0-15	3.2	1238.1
(n=10)	15-35	0.09	67.8
	35-65	Trace	2.3
	65-80	No detected	0.5

The concentration of organic dyes in the subsurface soils at a depth of more than 65 cm was significantly lower than that in the surface soils (Table 3). No matter how high the concentration of organic dyes in the surface soils, the concentration of organic dyes in the subsurface soils was still low. There was more than 195 times' difference between the two. Most organic dyes were thus accumulated in surface soils. According to the results, it can be concluded that the ability of the downward movement of organic dyes in soils is weak and the risk of pollution of groundwater by organic dyes is small.

The above law was further testified by soil-column modelling (Table 4).

Table 4. Vertical distribution of reactive X-3B red dye in soil-column modelling

Sampling site	Soil type	Depth (cm)	Concentration in collected solution	Concentration in soil
Tianjin	Drab soil (n=3)	20	7.4	38.3
		40	3.9	18.4
		60	1.2	7.1
		80	0.6	2.3
		100	0.04	0.3
Suzhou	Paddy soil (n=3)	20	9.1	29.3
		40	5.4	14.8
		60	2.9	7.9
		80	0.5	2.1
		100	0.05	0.8
Shaoxing	Red soil (n=3)	20	11.3	22.5
		40	6.8	12.8
		60	3.5	8.4
		80	0.9	3.9
		100	0.2	1.5
Ningbo	Paddy soil (n=3)	20	8.7	32.4
		40	5.6	12.3
		60	2.1	6.8
		80	1.3	2.3
		100	0.1	0.5
Guangzhou	Red soil (n=3)	20	12.4	20.5
		40	6.2	11.9
		60	2.9	6.3
		80	1.4	2.9
		100	0.3	0.7

The concentration of reactive X-3B red dye in all the tested soils at the depths of 0-20 cm was significantly higher than that in the initial leaching solution due to soil adsorption (He *et al*, 1998). The concentration of reactive X-3B red dye in the solutions collected at the bottom of soil columns was only 0.04-0.3 mg l^{-1}, with variance depending on soil types.

Some organic chemical compounds can be directly absorbed and utilized in molecular forms by plants (Clonic *et al.*, 1987). This was further proved by our analyses because it was not a small amount of organic dyes, including reactive X-3B red dye, that was absorbed into plants (Table 5). The average concentration of total organic dyes in watermelon and lotus root was up to 64.3 and 46.1 mg kg^{-1} dry weight, respectively. The average concentration of total organic dyes in radish and potato was also high. Many crops have great ability to absorb organic dyes from soils. Thus, there is no denying the fact that organic dyes can be transported from soils to plants in molecular forms. However, the transporting mechanism remains unclear.

Table 5. Organic dye concentration in polluted crops

Sampling site and crop	Reactive X-3B red dye (mg kg^{-1}) Average	Range	Σ(Organic dyes) (mg kg^{-1}) Average	Range
Jinzhou:				
Soybean			0.8 (n=10)	0.01-1.7
Potato			12.9 (n=10)	4.3-29.7
Tianjin:				
Wheat			1.3 (n=10)	0.1-2.8
Potato	0.03 (n=10)	0.01-0.1	10.8 (n=10)	6.4-16.8
Suzhou:				
Rice	0.09 (n=10)	0.01-2.3	2.1 (n=10)	0.6-3.8
Shaoxing:				
Rice	0.1 (n=10)	0.05-0.6	4.4 (n=10)	2.6-7.9
Radish	1.7 (n=10)	1.2-2.8	28.2 (n=10)	18.7-39.9
Watermelon	7.3 (n=10)	6.7-11.3	64.3 (n=10)	60.3-78.7
Ningbo:				
Rice	0.3 (n=10)	0.1-0.5	3.4 (n=10)	1.3-3.8
Soybean	0.9 (n=10)	0.7-1.6	5.2 (n=10)	4.9-5.7
Xiamen:				
Rice			0.8 (n=10)	0.1-1.9
Lotus root			46.1 (n=10)	8.3-126.4
Guanzhou:				
Radish	0.3 (n=10)	0.01-0.9	22.1 (n=10)	16.3-33.1
Celery			1.3 (n=10)	0.1-2.8

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