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Predicting Drifting Polystyrene Degradation in World Oceans Based on Thermal Decomposition

Hideki Kimukai, Koshiro Koizumi, Hiroyuki Taguchi, Akifumi Okabe, Kohei Takatama, Seon Yong Chung, Bum Gun Kwon, Masahiko Nishimura, Sibel Mentese, and Katsuhiko Saido*

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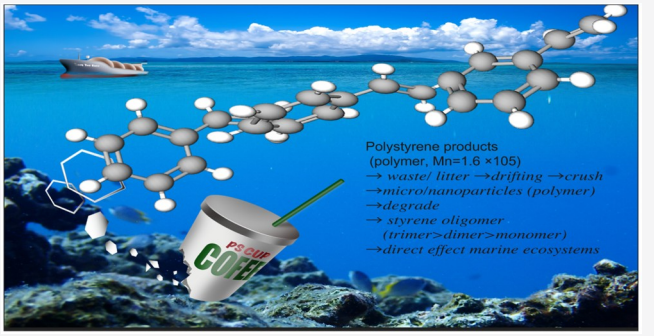
ABSTRACT: The accumulation of plastic litter in natural environments has become a serious global issue. Since 1972, mega to micro/nanosized drifting plastics have been determined to be highly a significant pollutant in all oceans worldwide. To clarifying numerous problems such as entanglement or improper ingestion due to drifting and debris plastic, the amounts of currently drifting plastics should be determined. For this purpose, chemicals derived from polystyrene (PS) degradation were analyzed for 4000 sand and water samples taken from around the world including open sea sites (surface to 5000 m depth) during the period from 2000 to 2018. All styrene oligomers (SOs) of styrene (styrene monomer, SM), 2,4-diphenyl-1-butene (styrene dimer, SD_2), and 2,4,6-triphenyl-1-hexene (styrene trimer, ST) were found to contain products from PS degradation. On the basis of survey SO values, 1.4×10^9 metric tons (MT) of SO were found to have been released into world oceans between 1950 and 2018. This SO subsequently underwent conversion to 2.7×10^6 MT of PS. Twenty percent underwent degradation, while 1.2×10^7 MT of PS apparently continued to drift about in ocean water. Drifting PS has been clearly shown not only to be crushed into micro/nanoplastic particles but also to degrade into basic structural units of SOs constituting PS.



KEYWORDS: *drifting plastic, polystyrene, degradation, styrene oligomer, toxicity*

1. INTRODUCTION

In addition to its outstanding features of lightness, low cost, great strength, and beauty, plastic can be molded into any desired shape and be produced in large quantities. It has thus come into wide use as a material indispensable for modern life. The cumulative amount of all plastics produced from 1950 to 2018 has been calculated as 7.0×10^9 metric tons (MT).[1,2] Whether accidentally or intentionally, waste plastics from land sources ultimately make their way into world oceans. To assess the hugh extent of this pollution, the amounts of plastics currently adrift should be determined. Polystyrene (PS) is one of the plastics present in largest amounts, and a significant constituent of drifting plastic floats on the surface of ocean water, thus making its presence obvious. PS was examined in this study to clarify the fate of ocean plastics in general.

In 1972, Carpenter and coworkers[3,4] reported in their survey that the number of floating plastic pieces is 3,500 with an average weight as much as of 290 g km^2 on the surface of the western Sargasso Sea. van Sebille et al.,[5] Cozar et al.,[6] and Eriksen et al.[7] calculated that between 7.0×10^3 and 2.7×10^5 MT of plastic debris are present on ocean surfaces as the predominant constituent of "garbage patches" in all world oceans.[8,9]

By 2050, debris plastics in the oceans may possibly weigh as much as or even more than all fish in the oceans.[10] Drifting plastics have been shown to exert two major effects on marine biota: entrapment of marine animals[11−14] and their improper ingestion as food.[15−19] A broad spectrum of marine animals from plankton to whales and seabirds has proven to succumb to injury due to microplastics (1 μm−5 mm) and nanoplastics (<1000 nm)[20−22] present in the digestive tract.[13] Thermoplastics produced from petroleum as raw material have been shown to be lipophilic. Thus, DDT, PCBs, and dioxins are all persistent organic pollutants (POPs) adsorbed in concentrated amounts on plastic. Drifting plastics thus serve as media for the enhancement of bioconcentrations of toxic chemicals.[23,24]

For the determination of PS due to styrene oligomers (SOs) generated by PS degradation,[2] over 4,000 sand and water samples from coastlines and open oceans, from the surface to

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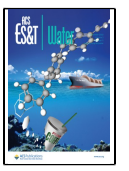

5,000 m deep, and from 26 countries and isolated islands were examined at different times. All samples were shown to contain SOs, bisphenol A (BPA), and phthalate (PAE).[25−28]

On the basis of surveyed SO and amounts of seawater, degraded PS in the oceans was estimated to be 2.7×10^6 MT from 1950 to 2018. Assuming a 3% waste PS inflow[29] in oceans, 20% PS was estimated to be degraded with 1.2×10^7 MT of PS presently adrift. Plastics such as PS are macromolecules and difficult to metabolize in organisms, but SOs dissoluble in water[30] are easily consumed and metabolized by organisms.

This is the third study on pollution due to plastic degradation not only for micro/nanoplastic particles but toxic chemicals in all world oceans.

2. MATERIALS AND METHODS

2.1. Reagents. Dichloromethane (DCM) for extraction of SOs was of reagent grade and manufactured by Wako Pure Chemical Co (Osaka, Japan). The internal standard, phenanthrene (PH), and surrogate, biphenyl (BP), was used after being purified using a special grade from Kanto Chemical Co., Inc. (Tokyo, Japan) following sublimation treatment. Styrene monomer (SM) and 1,3-diphenylpropane (SD_1) from Wako Pure Chemical Co. (Osaka, Japan) were used after the distillation of reagents prior to use. Styrene dimer (SD_2) and styrene trimer (ST) were prepared by the decomposition of PS and purified by distillation under reduced pressure by boiling point fractionation.[31] The purity of SD_2, ST, was determined by gas chromatography (GC) with a flame ionization detector (H-FID, CG-9A, Shimadzu, Kyoto) as 99.8% or more before use.

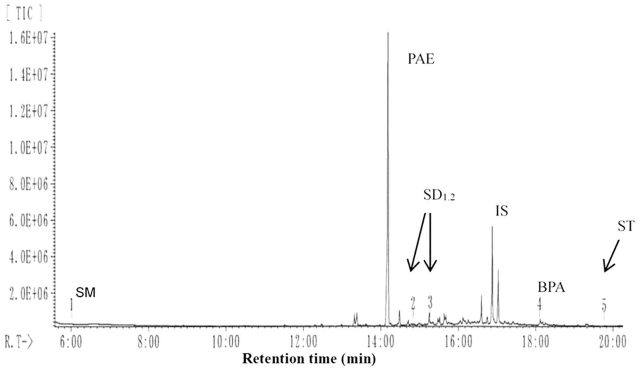

Figure 1. TIM -GC/MS chromatogram of Show Base pebble extractant in Antarctic, 1980. Identified chemicals: (1) styrene monomer, (2) 1,3-dipenyl- propane (styrene dimer), (3) 2,4-diphenyl-1 butene (styrene dimer), (4) bisphenol A(BPA), (5) 2,4,6-triphenyl-1-hexene (styrene trimer), and (6) internal standard (PH). The largest peak is phthalic acid ester (PAE).

2.2. Methods and Apparatus. Here, 5.0 g of beach sand and 2.5 L of water samples from coastlines or 10 L of water samples from the open ocean were examined.[22] The water samples were extracted on site using 100 mL of DCM with surrogate BP. After freeze-drying the sand overnight, 5.0 g of sand extracted using 10 mL of DCM was surveyed at different time periods. Following the addition of PH to each sample, 1 μL of the solution was injected into GC/MS with a microsyringe and analyzed. The GC used was HP6890 (Agilent Technologies, Inc., Santa Clara, CA, USA). The mass spectrometer (MS) was a JMS-AMII manufactured by Jeol, Ltd. (Tokyo, Japan). The separation column was DB-1(L, 30 m; ID, 0.32 mm; film thickness, 0.25 μm) manufactured by Agilent J&W. The details for GC and MS[2] are shown in Figure 1.

3. RESULTS AND DISCUSSION

3.1. Accuracy. The mass spectrum obtained by GC/MS, total ion monitor (TIM), was used to determine the fragment ion (m/z) of the target chemicals (SM, SD_2, ST). For quantitative analysis of the target chemicals by MS, selected ion monitoring (SIM), the following data were used: monitoring ions Q (quantitative ion), m/z: 104, 154, 178, 196, 208, 312, and I (qualitative ion), m/z: 78, 105, 117, 152, 193 ions. Calibration curves were prepared by the internal standard method using the detected ion peak area ratio (I/Q). It was thus possible to obtain very low concentrations (10^{-9} level) of SOs by SIM-GC/MS. When surrogate BP was added to DCM, the recovery was from 90.3% to 97.8%. The average was 95.2% or more, and the RSD was within 7.3%. A standard solution of each chemical (SM, SD_2, ST) was prepared to obtain a target solution using a pipet and a 10 mL volumetric flask, and the calibration curve of each chemical was prepared. Curve linearity ranged from 0.2 μg to 10 mg kg^{-1} with a correlation coefficient of $r = 0.9996-0.9999$. The detection limit was found at S/N = 2 to be 10 μg kg^{-1}. The detailed methods were shown previously.[2]

3.2. Analysis in Field and Commercial Products. Since 1972, debris plastics have been thought to remain in the marine environment forever.[3,4] Since 2000, current research has reported that these drifting plastics are crushed by the action of waves and light and made finer such as into micro/nanoplastic particles.[32−35] These generated particles have the same physical properties as the virgin resin (nurdle) pellets. Where is all the plastic?[42]

Table 1. Levels SOs Remaining (mg kg^{-1}) in Commercial Products Sampled in Some Countries

		SM		SD		ST		SOs
Country	Number of samples	All	Average	All	Average	All	Average	Average
Japan	30	77.1	2.57	44.1	1.47	651	21.7	25.7
Korea	20	23	1.15	45.8	2.29	738.4	36.9	40.3
China	20	20	1	21	1.05	360	18	20
Italy	10	11.2	1.12	8.2	0.82	1.7	0.17	2.1
Spain	5	6.75	1.35	4.35	0.87	7.35	1.47	3.7
Greece	5	3.7	0.74	6.6	1.32	0.8	0.16	2.2
USA	10	15.4	1.54	42	4.2	35	3.5	9.2
Total	100							
SO total		157.2		172.1		1794.3		
Ratio of SM:SD:ST		1		1.1		11.4		

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Table 2. Mean SO Values in Sand ($\mu g\ kg^{-1}$) and Water ($\mu g\ L^{-1}$) Sampled in Various Countries in the World

Site No.	Site	Number of Sample: Sand	Number of Sample: Water	Average level of Styrene Oligomer: Sand ($\mu g\ kg^{-1}$)	Average level of Styrene Oligomer: Water ($\mu g\ L^{-1}$)
1	United Kingdom	40	11	390	3.97
2	France	4	1	450	1.2
3	Portugal, São Miguel Island	60	15	270	1.3
4	Spain, Tenerife Island	60	15	1140	1.2
5	Italy, Sardinia Island	68	17	380	0.5
6	Tunisia	32	8	92	3.3
7	Croatia	8	2	15	1.7
8	Slovenia	12	3	31	0.2
9	Greece, Salamis, Aigina, Crete Island	40	10	31,400	1.4
10	Turkey	44	15	2400	2.8
11	Egypt	8	2	320	1.4
12	India, Elephanta, Kanniyakumari	60	25	940	4
13	Sri Lanka	40	15	238	11.5
14	Malaysia, Penang Island	60	15	18,900	4
15	Vietnam	40	10	440	3.4
16	Philippines, Luzon, Mindanao	40	10	150	2
17	Taiwan	40	10	150	13
18	China, Hong Kong Island	32	10	1410	10
19	Korea, Cheju Island	120	40	580	6
20	Japan:				
20−01	Honshu, Isolated Island (Ogasawara, Iriomote Ishigaki, Tsuhshima, Oki, Sado)	1601	307	700	2.4
20−02	Open ocean (see Tables 3 and 4)		300		0.2
21	United States				
21−01	Alaska, Aleutian Islands (Unalaska, Popof)	41	12	20	0.1
21−02	Washington	40	10	510	30.4
21−03	Oregon	40	10	820	22
21−04	California, Catarina Island	60	15	2,910	1.3
21−05	Massachusetts	40	10	7370	6.9
21−06	New Jersey	40	10	159	3.5
21−07	Virginia	8	2	450	4.5
21−08	Florida, Key Largo, Key West, Conch Key	60	15	23,500	8.75
21−09	Texas	60	15	500	5.7
21−10	Puerto Rico	60	15	350	0.8
21−11	Oahu, Kauai, Maui, Hawai'i	120	60	16	0.02
22	Guam	32	8	1499	4.3
23	Micronesia, Pohnpei	20	7	390	0.9
24	Costa Rica	28	7	2630	8.4
25	Bermuda	32	8	1200	3.7
26	Mexico	48	10	1600	5.7
	Total	3138	1055	104,320	182
	Average SO (all) values			1774.7	4.5
	Composition ratio SM:SD:ST			1:1:8	1:1:8

We have been conducting research to elucidate the decomposition mechanism of thermoplastics.[2,36−40] As a result, it was clarified that one MT of PS decomposes 0.3 g per year at 30 °C to generate SO.[2] Here, 5 g of Antarctic pebbles stored in glass bottles since 1980 was extracted with DCM and analyzed using TIM-GC/MS. The SOs and other chemicals, such as BPA and PAE, were quantified. The result is shown in Figure 1.

As shown in Figure 1, SM has been found as a breakdown product formed by cinnamon mold flora and may also be present in oceans as a single contaminant.[41] However, SOs with constant ratios of SM:SD:ST = 1:1:5 do not occur naturally and are therefore degraded products from PS.[2,36,37] As shown in Figure 1, detected chemicals may be derived from plastics degradation. BPA was derived from PC[38] or EPX,[39] and PAE was from polyvinyl chloride (PVC) plasticizer[40] and polyethylene terephthalate (PET).

SO contaminants were detected in commercial PS products such as disposable lunch boxes, food trays, and noodle containers sold in various countries as shown in Table 1.

The SO composition ratio is SM:SD:ST = 1: 1.1:11.4 in Table 1. The detected SO values are different for each country. It is pointed out that these differences may reflect the PS synthesis for nurdle pellets and the heat treatment at the molding process. The SO composition ratios in field surveys from around the world had a range for sand and water samples around SM:SD:ST = 1:1:8 as shown in Table 2.

The composition ratios of purified PS (SO-free PS, $M_n = 1.6 \times 10^5$, $M_w = 5.2 \times 10^5$, $M_w/M_n = 3.3$) thermal decompositions at 30° to 250 °C were shown as SM:SD:ST = 1:1:5. These results clearly show that drifting PS is the source of SO in the ocean. The inflowed PS from land-based plastics were crushed into micro/nanoplastic particles first, then degraded to SO molecular pieces and dissolved in water.[30]

3.3. Field SO Survey in World Oceans. Studies on drifting/debris plastic contamination have been conducted by using ships and drawing a collecting net[3−9] or observing the movement of lump plastics using satellites, then estimating drifting plastic by statistical methods.[42,43] These studies are only observations on the surface of the ocean and are considered important for detecting the movement of drifting plastics and contaminated areas. When plastics drift in the ocean, how plastics undergo chemical change is little known. In this study, generated SO from drifting PS degradation in the world ocean was observed. This SO pollution is invisible to the naked eye, but unlike plastic lumps, SO is thought to be dissolved and dispersed in water.[30] It is important to understand what kind of environmental factors exist in the ocean for SO generation or elution from PS.

Figure 2 shows each surveyed country (1) UK to (26) Mexico cycles and (21) USA/a, Alaska to USA/k, Hawaii, cruise line (KH12-3, red line; sampling station, white circle), garbage patches (yellow, green circles), and ocean currents (yellow arrow). Over 4000 sand and water samples taken from coastlines and the open ocean, including from the surface to a 5000 m depth, and from 26 different countries and isolated islands were surveyed at different time periods, and SO was analyzed: (3) São Miguel, (4) Tenerife, (5) Sardinia, (9) Salamis, Aigina, Crete, (12) Elephanta, Kanniyakumari, (14) Penang, (16) Mindanao, (18) Hong Kong, (19) Cheju, (20) Ogasawara, Iriomote, (21−01) Aleutian Islands, (21−04) Catarina Island, (21−08) Key Largo, Key West, Conch Key, (21−11) Hawai'i, (22) Guam, (23) Micronesia, and (25) Bermuda. Drifting and on-shore debris plastics were visibly observed on all surveyed coasts.

The mean SO values from the coastal surveys worldwide were found to be 1774.7 $\mu g\ kg^{-1}$ for sand samples and 4.5 $\mu g\ L^{-1}$ for water samples as shown in Table 2. SOs were also detected from the open ocean in the Northwest Pacific Ocean in the order of

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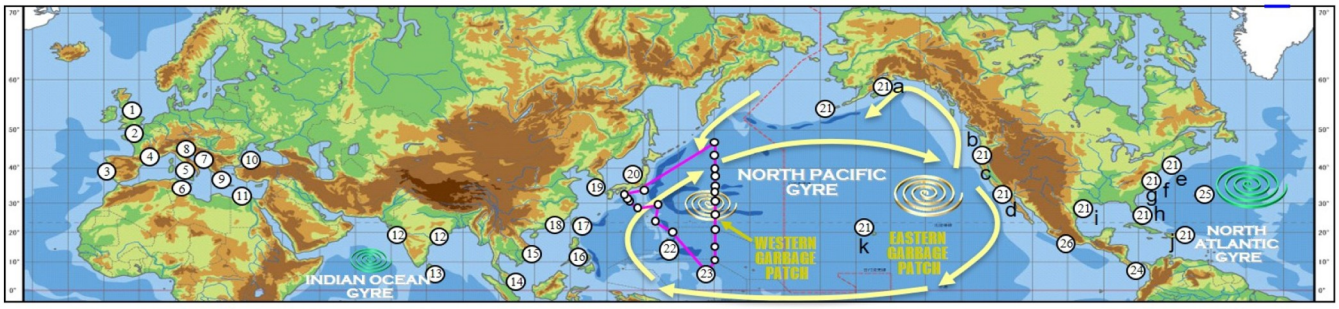

Figure 2. Survey countries for 1−26 (number in a circle and 21-a to 21-k), cruise line (KH12-3, white circles along red line), ocean current (yellow line), and ocean garbage patches (yellow and green circles). The country name is shown in Table 2 with the site number.

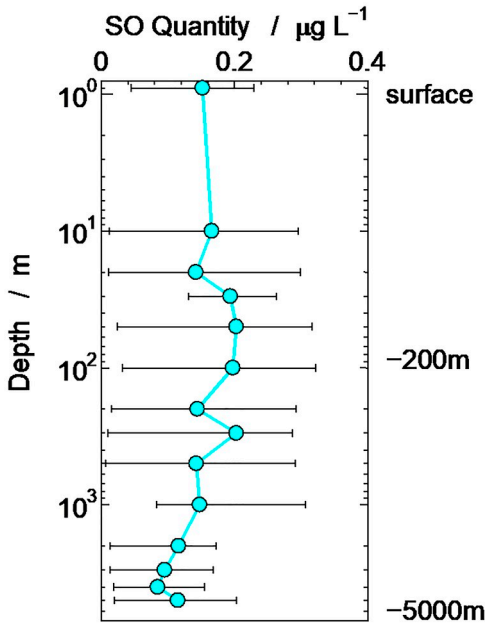

Figure 3. Vertical SO values in the pelagic ocean. Distributions of SOs from the surface to a 5000 m depth during sampling cruise (KH12-3, July 6 to August 14, 2012) in the open ocean (10° to 45° N; 133° to 160° E). Notes: Photic zone, turbulent mixing to 1000m; water depth on the left axis is shown in a log scale.

0.2 μg L^{-1} at the surface, and at depths of 2000 to 5000 m, the values were 0.1 μg L^{-1}.

The highest regional value of SOs in sand samples was for Greece at 31,400 μg kg^{-1} (Table 2, site 9) and for water was Washington/USA at 30.4 μg L^{-1} (Table 2, sites 21−02). The area with the lowest SO levels of 16.0 μg kg^{-1} for sand and 0.02 μg L^{-1} for water was in the Hawaii Islands (Oahu, Kauai, Maui, Hawai'i)/USA (Table 2, site 21−11).

SOs in the Northern Hemisphere are present in relatively small amounts at high latitudes where land and water surface temperatures are low, such as in Ullapool (United Kingdom, 57.89′ N, Table 2, site 1), Sand Point and Dutch Harbor (Alaska, United States, 55.20′ N, 53.53′ N, Table 2, site 21−01 both), but in large amounts at low latitudes such as in Matara (Sri Lanka, 5.55′ N, Table 2, site 13), Port Dickson (Malaysia, 2.32 ′N, Table 2, site 14), and Limon and Puerto Soley (Costa Rica east side, 9.98′ N, west side, 9.93′ N,Table 2, site 24 both). Beach sand is exposed directly to the Sun; consequently, the surface temperatures of shallow coastal areas may reach as high as 60 °C during the day in tropical and subtropical areas, thus promoting PS degradation.[2,36]

High values of SOs were found to be present along coastlines near large cities including London/UK, Tokyo/Japan, and Los Angeles and Boston/USA, where human population densities are large. Comparing the SO levels on the East Coast (Table 2, sites 21−02, 21−03, 21−04, Pacific Ocean) and West Coast (Table 2, sites 21−05, 21−06, 21−07, Atlantic Ocean) at the same latitude in the United States (USA), the East oast is 2 times higher in sand samples but 3.6 times higher in water samples than the West Coast. However, in the case of isolated islands such as São Miguel (Portugal, 37.48 ′N, Table 2, site 3), Hamilton (Bermuda, 32.30′ N, Table 2, site 25), and Pohnpei (Micronesia, 6.92′ N, Table 2, site 23), SOs were shown to be present at low values and may have been derived solely from PS debris.

3.4. SO in the Open Ocean. As shown in Table 2, the coastal region SOs in water and sand were affected by the latitude, longitude meteorology, ocean currents, weather,[44−46] and population density. Results on isolated islands that may be less affected by these factors, such as population or industry, are from inland. Therefore, an open ocean SO survey was conducted from surface to bottom water. Using the Japanese Government research ship *Hakuho* along the 160° E longitude, 5000 km north to south and 2000 km east to west, during the KH12-3 cruise, in 2012, in the Northwest Pacific Ocean, SOs were surveyed from surface to bottom with 10 L of water at a fixed depth each (Niskin water sampler/General Oceanics, Inc.). The cruise is shown by the red line and sampling stations (Stn) shown white circles in Figure 2. Results are shown in Figure 3 and Tables 3 and 4. The cruising details and surface SO are shown in Table 4.

Table 3 shows the deep sea SO result. In Figure 3, the depth of the sea is shown logarithmically on the vertical axis (left/m), and the SO value detected at each depth is shown in μg L^{-1} on the horizontal axis. The mean surface current was 0.7 knots during this cruise as shown in Table 4. SOs tend to be high in the photic zone at a depth of 200 m as shown in Figure 3, but at more than 2000 m where there is only minimal horizontal currents and therefore more limited water mixing, mean SO levels are approximately 0.1 μg L^{-1}. The SOs would thus appear to adhere or be adsorbed by organic or inorganic materials, and this flocculation to particulate matter may be a mechanism for its vertical movement. In the deep sea, SOs were two times as high at Stn-9 and 5 times higher at Stn-8 than at the surface as shown in Table 3. This area is the same as the Northwest Pacific Garbage Patch. The SOs composition ratio in field surveys from around the world had a range with sand and water samples of around SM:SD:ST = 1: 1:8 as shown in Table 2; these values are basically in the same range as those found for the samples around Japan.[28]

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Table 3. Deep Sea SO Values (ng L^{-1}) and Composition during KH12-3 Cruising

	Depth 2000 m				Depth 3000 m				Depth 4000 m				
Sampling site[a]	SM	SD	ST	SO	SM	SD	ST	SO	SM	SD	ST	SO	Salinity (per mL)
Stn-1	0.4	26.2	133.6	160.2	1.3	9	126.2	136.5	1.1	29.3	26.7	57.1	37.8
Stn-5	0.3	4.1	141.7	146.1	0.3	13.1	118.2	131.6	0.3	23.4	124.6	148	37.3
Stn-9	0.6	17.6	154.5	172.7	0.3	34.3	144.9	179.5	0.5	18.5	158.4	177.4	36.4
Stn-12	0.2	24.2	104.5	128.9	0.3	3.6	120.3	124.2	0.2	6.7	87.1	94	37.1
Stn-15	0.4	13.2	97.9	111.5	0.9	16.7	114.6	132.2	1.1	5.1	110.5	116.7	36.7
Stn-16	0.1	53.8	38.8	92.7	0.5	30.2	26.6	57.3	0.2	18.6	11.2	30	36.7
Total	2	139.1	671	812.1	3.6	106.9	650.8	761.3	3.4	101.6	518.5	623.2	222
Average	0.3	23.2	111.8	135.4	0.6	17.8	108.5	126.9	0.6	16.9	86.4	103.9	37.0
±S.D.	0.2	17.0	41.9	30.2	0.4	12.1	41.5	39.4	0.4	9.4	57.3	55.2	0.5
Composition ratio													
	Depth 2000 m				Depth 3000 m				Depth 4000 m				
SM:SD:ST	1	70	339		1	30	181		1	30	153		
Total SO	SM: 9	SD: 347.6	ST: 1840										
SM:SD:ST	1	39	204										

[a]Stn: Sampling station.

Table 4. SO Contamination (ng L^{-1}) on Cruising KH12-3 from Surface Water during July 6 to August 14, 2012

Sampling station	Date	Latitude (N)	Longitude (E)	SO total (ng L^{-1})	SM (ng L^{-1})	SD (ng L^{-1})	ST (ng L^{-1})	Surface temp. (°C)	Water temp. (°C)	pH	Salinity (per mL)	Flow (knot)
Stn-1	10-Jul	46°555.100′	159°59.8176′	157	0.5	25.6	131	8.1	8.9	8.04	32.8	0.4
Stn-2	12-Jul	43°30.169′	160°00.139′	147	0.6	14.1	132	14.0	13.3	7.96	32.9	0.5
Stn-3	13-Jul	39°59.995′	159°59.7917′	154	0.7	19.8	133.3	19.1	16.9	8.20	33.4	0.9
Stn-4	14-Jul	37°30.0835′	160°00.1599′	161	0.3	21.4	139	22.4	21.3	8.03	34.1	0.6
Stn-5	14-Jul	34°59.9444′	100°00.3908′	199	0.7	69.1	129	25.2	24.3	8.05	34.5	1.6
Stn-6	16-Jul	33°00.0618′	159°59.8779′	162	0.5	21.3	140.4	26.0	24.3	8.02	34.7	0.3
Stn-7	17-Jul	30°01.1139′	159°58.4579′	174	0.4	25.3	148.4	27.6	26.8	8.03	34.8	1.1
Stn-8	18-Jul	24°59.0949′	159°59.9460′	942	0.7	53.6	887.3	28.7	28.1	8.08	35	0.3
Stn-9	19-Jul	20°00.9884′	159°59.4324′	181	4	12.9	163.6	28.6	28.5	8.09	35	0.5
Stn-10	22-Jul	14°58.9970′	159°59.0250′	124	0.3	23.9	99.8	28.2	28.5	8.06	35.4	0.3
Stn-11	24-Jul	10°00.2840′	159°59.7093′	123	0.3	4.4	118	28.5	28.3	8.08	35.8	0.7
Stn-12	1-Aug	20°00.7549′	148°00.7702′	131	0.3	0.3	127.6	25.9	28.4	8.13	35.6	0.5
Stn-13	5-Aug	24°00.4415′	143°12.8222′	133	0.3	8.5	124.2	28.2	28.6	8.18	34.7	0.2
Stn-14	6-Aug	29°59.0387′	144°50.4752′	230	0.2	4.9	224.6	27.2	26.8	8.06	34.5	0.6
Stn-15	8-Aug	27°59.3591′	138°00.1555′	126	0.3	5.9	119.6	27.9	27.1	8.10	34.3	0.6
Stn-16	9-Aug	31°00.0244′	134°04.2201′	135	0.3	4.4	130	28.0	27	8.07	34.3	1
Stn-17	10-Aug	32°15.2999′	133°23.8904′	139	0.5	6.1	132.6	28.5	27.4	8.16	34.2	1.6
Stn-18	11-Aug	33°48.8382′	133°39.9826′	133	3	11.9	121.2	27.6	25.9	8.18	33.5	0.7
Total				3551	13.9	333.4	3201.6					
Average				197.3	0.77	18.5	177.9	25.0	24.5	8.1	34.4	0.7
Ratio of SM:SD:ST = 1:24:230					1	24	230					

In Tables 3 and 4, the SO composition ratio was SM:SD:ST = 1:24:240 at the surface, and the deep sea ratio (2000 m or more) was SM:SD:ST = 1:39:204. PS degradation first generated ST at the rate-determining step.[2] This ST is further decomposed to SD and SM.

All substances are finally metabolized by microorganisms. We had isolated the 2,4,5-T degrading bacteria.[47] The SM degrading microbes were isolated,[48] but SD_2 and ST degrading bacteria do not isolate for 20 years, until now.[49] In the open ocean, the ST degradation speed was very slow. The ST remained in the ocean, and the SO composition ratio was changed, but this is the PS main degradation pathway.[2,36,37]

3.5. PS Inflow and Drifting PS. To consider countermeasures for plastic pollution in the ocean, understanding the global mass of inflow and drifting plastic is very important. Moore et al.[50] reported 334,271 plastic pieces with a weight of 5114 g km^2 to be present in the North Pacific Ocean, and the amounts of drifting plastic to increased by 10 times as much between 1972 and 2001. Jambeck et al.[29] estimated total waste plastics inflow in 2010 into world oceans to range from 4.8 to 12.7×10^6 MT. Drifting micro/nanoplastic particles tend to sink and change properties over time due to weathering, embrittlement, fragmentation, and POPs absorbing.[23,24] However, this estimated value may not be entirely accurate, and reliable data for degraded/sedimented plastics in oceans is almost nonexistent. As shown in Table 2, the SO data for all sampling sites had significant effects on SO values such as location (latitude, open or closed-sea) and weather.

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This study determined only amounts of drifting PS from a SO field survey and the extent of its discharge into the oceans throughout the world. The amount of waste PS inflow accumulated in ocean bodies from 1950 to 2018 have been estimated as 1.5×10^7 MT,[2] assuming PS to constitute 7% of plastic global total production (4.8×10^8 MT) and 3% of plastics[29] to flow into world ocean.

Using open ocean deep sea SO values of 0.1 μg L^{-1} and the total water volume in oceans as 1.4×10^{21} L, it was determined that 1.4×10^9 MT SOs entered the oceans between 1950 and 2018. The conversion of SO to PS has been calculated as 2.7×10^6 MT. From 1950, 1.5×10^7 MT of waste PS inflow entered the ocean, with 20% of drifting PS degraded to SO and 1.2×10^7 MT of debris PS currently drifting.

Chemicals such as SOs[51] from PS, BPA[52] from PC or EPX, and PAE[53] from plasticizers of PVC or PET are generated in the temperature range from 30° to 50 °C.[2,38−40] Unlike plastics (macromolecules), these chemicals are soluble in water and exert direct toxic effect on marine ecosystems.

4. CONCLUSIONS

It has been thought that drifting plastics do not break down under natural conditions but remain permanently in oceans. Recent studies have been directed to the phenomena of plastics crushing into fine micro and nanoparticles. The present authors have derived a new decomposition system for thermoplastics from ambient temperatures. Due to SO-free PS decomposition, PS was shown kinetically to decompose at 30 °C to generate SO and as much as 300 MT of PS may have decomposed since 1950. To account for the significant difference between surveyed SO and the SO-free PS decomposition, physical factors that promote PS decomposition in oceans must be taken into consideration. Drifting plastic has been proven as the source of toxic chemicals in world oceans.

This study clearly indicates generated monomers to be quite likely noxious and harmful to marine biota directly. This third study on new pollution indicates quite strongly the possibility that these chemicals from degraded plastic will continue to increase and thus should be considered not only just a due and but serious threat to marine ecosystems worldwide.

AUTHOR INFORMATION

Corresponding Author

Katsuhiko Saido − *Albatross Alliance, Honolulu, Hawaii 96826, United States; Albatross Alliance, Katsushika, Tokyo 1240012, Japan; College of Science and Technology, Nihon University, Chiyoda, Tokyo 1018308, Japan;* orcid.org/0000-0002-8797-8794; Phone: +81-8054376718; Email: katsu.saido@gmail.com; Fax: +81-336915579

Authors

Hideki Kimukai − *Albatross Alliance, Honolulu, Hawaii 96826, United States*

Koshiro Koizumi − *College of Science and Technology, Nihon University, Chiyoda, Tokyo 1018308, Japan*

Hiroyuki Taguchi − *School of Pharmacy, Nihon University, Funabashi, Chiba 274855, Japan*

Akifumi Okabe − *College of Science and Technology, Nihon University, Chiyoda, Tokyo 1018308, Japan*

Kohei Takatama − *Advanced Institute for Computation Science, RIKEN, Kobe, Hyougo 2778564, Japan*

Seon Yong Chung − *Chonnam National University, Bug-gu, Gwangju 500757, South Korea*

Bum Gun Kwon − *Chonnam National University, Bug-gu, Gwangju 500757, South Korea*

Masahiko Nishimura − *Atmosphere and Ocean Research Institute, The University of Tokyo, Kashiwa, Chiba 2770882, Japan*

Sibel Mentese − *Çanakkale Onsekiz Mart University, Merkez, Çanakkale 17020, Turkey*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsestwater.2c00023

Author Contributions

K.S. and H.K. contributed to the total coordination of this project, field sampling, and chemical analysis. H.T., K.T., S.M., and A.O. contributed to the kinetic calculation of PS decomposition. K.K., S.Y.C., B.G.K., M.N., H.K., and S.M. contributed to field sampling and discussions.

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Notes

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DEDICATION

This paper is dedicated to UIC Emeritus Distinguished Professor Ananda Mohan Chakrabarty, who died 10 July 2020.

ACRONYMS AND ABBREVIATIONS

BP = biphenyl polystyrene
BPA = bisphenol A 2,2-bis(4-hydroxyphenyl)puropane
DCM = dichloromethane
DDT = dichlorodiphenyltrichloroethane
EPX = epoxy resin
MT = metric tone
PAE = phthalic acid ester
PC = polycarbonate
PCB = polychlorinated biphenyl
PET = polyethylene terephthalate
PH = phenanthrene
POP = persist organic pollutant
PS = polystyrene
PVC = polyvinyl chloride
SD_1 = styrene dimer 1,3-diphenyl-1-butene
SD_2 = styrene dimer 2,4-diphenyl-1-butene
SIM = selected ion monitor
SM = styrene monomer
SOs = styrene oligomer
ST = styrene trimer 2,4,6-triphenyl-1hexene
TIM = total ion monitor

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