

Research Article

Analysis of Drifting Polystyrene Degradation Surround Japan

Amamiya K¹, Koizumi K², Yamada K¹, Hiaki T¹, Kusui T⁴ and Saido K^{1,3*}¹College of Industrial Technology, Nihon University, Japan²College of Science & Technology, Nihon University, Japan³Albatross Alliance, Japan⁴Toyama Prefecture University, Japan

*Corresponding author: Katsuhiko Saido, College of Industrial Technology, Nihon University, Chiba, Japan

Received: January 09, 2020; Accepted: February 06, 2020; Published: February 13, 2020

Abstract

Due to accidental or intentional littering, plastics make their way into rivers and ultimately into oceans. No studies have been conducted on plastic decomposition at low temperatures in the ocean owing to the misconception that plastic hardly decomposes, if at all. To clarify if drifting plastics do indeed break down or not. Not only does this happen through micro/nano-scale fragmentation, but also potentially noxious chemicals are generated. To examine the level of chemical contamination of ocean bodies due to debris/waste Polystyrene (PS), 2,000 sand and water samples surrounding Japan were analyzed by GC/MS since 2,000 to 2015. All samples containing styrene oligomer (SOs) which consist of ethynylbenzene (Styrene Monomer, SM), 2,4-diphenyl-1-butene (Styrene Dimer, SD) and 2,4,6-triphenyl-1-hexene (Styrene Trimer, ST). The composition ratios were SM1: SD₁: ST 7 to10. Mega/Macro debris PS not only fragmented to generate micro/nano PS-particles (micro/nano plastic) but also chemically degraded to basic structure unite chemicals SOs.

One Sentence Summary: PS in the ocean breaks into its oligomer at ambient temperatures throughout the year, posing a serious threat to marine ecosystems.

Keywords: Marine debris plastic; Polystyrene; Degradation; Styrene ligomer; Contamination

Introduction

World plastic production had reached 1.5×10^6 metric tons (1,500 million kilograms) in 1950 and increased to 322×10^6 metric tons (322 billion kilograms) in 2015 [1,2]. Accidentally or intentionally, the release of this plastic waste from land sources will ultimately make its way to oceans all over the world [3-5]. Two types of plastic have been shown to have adverse effect on oceans—drifting plastic, which traps marine animals and causes digestive disorders [6,7] and acuminate persistent organic pollutants (POPs) in the plastic. Lebereton et al. confirmed that these plastics have been on the rise in ocean “garbage patches” [8] around the world. The POPs on the other hand are organic wastes that persist for long periods of time on the ocean surface [9,10]. Although plastics are durable, in oceans, they eventually undergo extensive chemical fragmentation into pieces less than 5 mm in diameter, which are called micro/nano-plastics [11,12]. These pieces are digested by the planktons [13,14]. Plastic fragments ingested by larger marine species and smaller plankton or accumulating elsewhere are still suspected of damaging the marine biota [15,16].

This research article presents a first-of-its-kind extensive study on the degradation of PS at sea surface temperatures. Over 2,000 sand and water samples taken from surrounding Japan at different time periods were analyzed for SOs which generated chemical degradation products of PS at ambient temperature. All the samples with PS were shown to contain SOs surround Japan coast lines.

Methods**Reagents/samples and analyzers**

The extractant Di Chloro Methane (DCM) to SOs from sand

and seawater, a pesticide analysis reagent manufactured by Kanto Chemical Co, Ltd. was used. For SM, a special grade reagent manufactured by Wako Pure Chemical Industries, Ltd. was used after purification by distillation. 2,4-diphenyl-1-butene (Styrene Dimer: SD₁) and 2,4,6-triphenyl-1-hexene (ST) decompose PS and purify by boiling fractionation under reduced pressure [5]. The purity of each reagent was analyzed by Gas Chromatography (GC) equipped with H-FID detector, and confirmed to be 99.8% or more were used. For 1, 3-diphenylpropane (styrene dimer: SD₁), a special grade reagent manufactured by Wako Pure Chemical Industries, Ltd. was used. The Phenanthrene (PT), internal standard and surrogate Substance Biphenyl (BP) were used after purifying a special grade reagent manufactured by Wako Pure Chemical Industries, Ltd. by a sublimation method. GC used in the analysis was HP6890 manufactured by Agilent, the Mass Spectrometer (MS) was JMS-AMII manufactured by JEOL Ltd., and the column was DB-1 manufactured by Agilent @ J & W. The analytical operating conditions were shown in Table 1.

Survey site and sampling method

In order to grasp the actual situation of SOs dissolved in seawater and sand in the coastal area of Japan, the survey site was selected for the 10-area corresponding by the Japan Ministry of Agriculture, Forestry and Fisheries for administrative management [18]. Dispatched four islands (Mainland/Hokkaido to kyushu) to the 1- to 9-reigon survey site. Considering the geographical factors of Japan, Okinawa and 12 isolate islands are separated from the administrative control (from the north: Rebun, Rishiri, Tobishima, Sado, Oki, Tsushima, Iki, Fukue, Hachijo, Ogasawara/Chichijima with Anijima, Ishigaki,

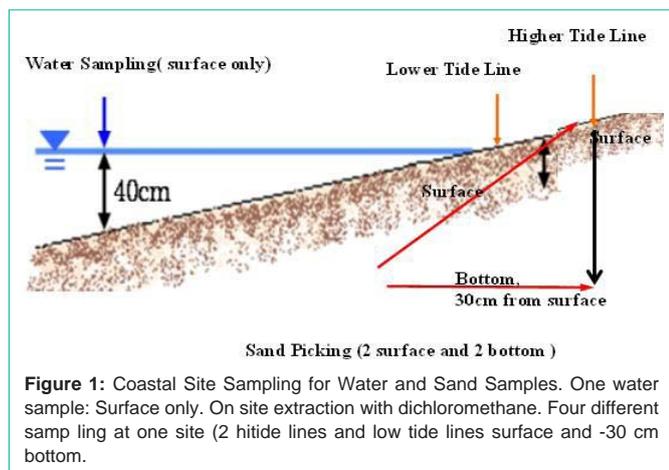


Figure 1: Coastal Site Sampling for Water and Sand Samples. One water sample: Surface only. On site extraction with dichloromethane. Four different samp ling at one site (2 hitide lines and low tide lines surface and -30 cm bottom).

Iriomote with Uchibanari and Sotobanari- island) as the 10- region. After visual inspection of the drifting plastic, sand and seawater samples were collected. The Coast Guard is published by the Japan Coast Guard (Ministry of Internal Affairs and Communications Statistics Bureau, Coastal Statistics), Environmental Vulnerability Index Map, download a total of 2,147 coastal topographic maps [19], read only the beach area using a Koizumi Sokki Kilvimeter (MAP-metercomcurve-10), The beach length was calculated to be about 5,000 km as shown in Table 2, which classified Japan Ministry of Agriculture, Forestry and Fisheries with prefecture (Table 2).

Sand collection and analytical preparation: The sand samples were collected at the surface of the high tide upper shoreline and directly below and at a depth of 30 cm, and at the surface of the lower beach and immediately below and at a depth of 30 cm. In other words, a single sample of sand was collected using a stainless-steel shovel to collect about 100 g of a total of 4 samples and stored in a glass container. The sand collected at the site was dehydrated by freeze-drying overnight in the laboratory, weighed 5.000 g precisely, added 1 mg kg⁻¹ of diphenyl, added 5 mL of DCM once, and irradiated with ultrasonic waves (once 30 seconds for 3times), extraction was performed with a total of 20 mL of DCM. The extract was concentrated using a rotary evaporator to just before drying, and an internal standard substance (phenanthrene) was added to the residue to a concentration of 5 µg kg⁻¹ at the time of measurement. Quantification was based on the internal standard method.

Seawater sampling and analytical preparation: Seawater samples were collected from surface water at a depth of 40 cm using a stainless beaker. Using a 1 L glass separatory funnel at a survey site, a total of 2.5 L of seawater filtered with a cotton plug (800 mL to 900 mL each time, JIS K 0450-10-10: 2000 compliant), 100 mL of DCM (Surrogate substance: diphenyl 1 mg kg⁻¹ added). The extract was stored in a glass container (Teflon packing).

The seawater extract collected in the field was separated into aqueous layers using a separating funnel, and the aqueous layer was re-extracted three times with 5 mL of DCM each time. The combined DCM layers were dried overnight with 10 g of anhydrous sodium sulfate. The extract was filtered to remove the desiccant, concentrated using a rotary evaporator until just before drying, and used as a GC/MS measurement after the same operation as in sand.

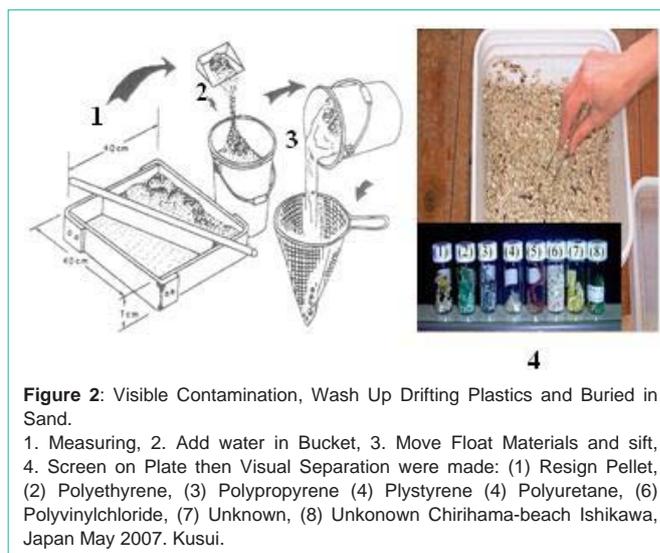


Figure 2: Visible Contamination, Wash Up Drifting Plastics and Buried in Sand.

1. Measuring, 2. Add water in Bucket, 3. Move Float Materials and sift, 4. Screen on Plate then Visual Separation were made: (1) Resin Pellet, (2) Polyethylene, (3) Polypropylene (4) Polystyrene (4) Polyuretane, (6) Polyvinylchloride, (7) Unknown, (8) Unkonown Chirihama-beach Ishikawa, Japan May 2007. Kusui.

In other words, the SO value evaluation at one survey site was performed using a total of five analytical samples, four for sand and one for seawater (Figure 1).

Results and Discussion

Visible survey

Isobe et al, garbage dumped from the coasts of Asia has drifted to the shores of Japan in about 7 to 10 days [20]. From 2009 to 2015, the Japan Ministry of the Environment is being conducted as 7-drifting coast model area bellow [21]: 1. Tsushima, Nagasaki/Prefecture (region-9), 2. Shimonoseki, Yamaguchi/Prefecture (region-4), 3. Hakui/Ishikawa Prefecture (region-4), 4. Satsuma/ Kagoshima Prefecture (region-9), 5. Awajishima/ Hyogo Prefecture (region-8), 6. Kamisu/Ibaraki Prefecture (region-5), and 7. Kyushu, Ishigaki, Okinawa/Prefecture (region-10).

The amount of washed up marine litter on the Japanese coast is estimated 220,000 to 590,000 metric tons (MT, weight, 2009 to 2013) per year, of which 30% is classified as artificial litter (plastic including wood, metal and glass). About 50% of artificial garbage is plastic. It is estimated that 1,400 to 3,900 MT are drifting from the estimated 4% of the drifting plastic is PS [22].

Lavender [12], Thompsom [23], Andrady [24], the drifting plastic that has flowed into the ocean is a large plastic lump (mega to macro-plastic) of more than 1m³, which is less than 5mm in size while drifting in the ocean. They point out that these macronized plastics are broken down into micro/nano-plastics and are taken up by small organisms such as plankton into the body [6,7]. Takada point out how microplastics may change over time, and that these plastics may absorb and concentrate POPs such as dioxins dissolved in the ocean, causing new pollution [9]. If drifting plastic drifts to the shore, it is observed that it will return to the ocean within one month due to the effects of tides and currents, but some will be buried and remain on the drifting shore [25]. Kusui et al. investigated plastics buried per unit volume at Chirihama, Ishikawa Pref. The result was shown in Figure 2.

The buried plastic collected during this survey was 8,000 cm³

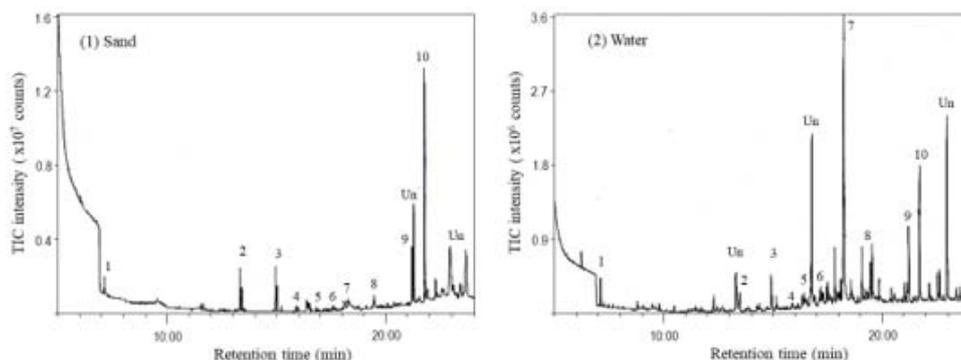


Figure 3: TIM-GC/MS chromatogram of the contaminate chemicals in (1) Iriomotejima and (2) Tokyo bay water samples.

(a) Monitoring and Sampling Sites with Ocean Currents (pink) and Seasonal Wind (blue) Surround Japan

Main Land: Five Island (Hokkaido, Honshu, Shikoku, Kyushu and Okinawa)

(b) Isolated Islands SO Contaminations Region 10, a to h

a: Rebun and Rishiri, b: Sado, c: Hachijyo, d: Tsushima, e: Fukue, f: Ishigaki g: Iriomote, h: Ogasawara

Table 1: GC/MS Apparatus and analytical conditions.

Apparatus	Jeol JMS - AM II with GC/MS : HP6890
Selected Ion (SI, m/z)	78.104.105.152.178.193.196.207.208.312
Injection	1 μ L
Column	DB-1 (L:30m, ID:0.32mm, Thick:0.25 μ m)
Injection, System	Splitless
Injection, Temp.	250°C
Column Temp.	40°C(5 min HOLD) _290°C up (Programrate: 15°C/min,290°C (5 min HOLD))
Interface Temp.	250°C
Ion Souce Temp	200°C
Ion Acceleration Current	70 eV
Current	300 μ V
PM Voltage	600 V
Carrier Gas	He (1.4 ml/min)

(40 × 40 × 5 cm, d = 2.5, weight approx. 30 kg), virgin resin pellets (mixture), Poly Ehylene (PE), Poly Propylene (PP), Poly Styrene (PS), 3.5 g of thermoplastics such as Poly Urethane (PU) and polyvinyl chloride (PVC) in Figure 2. It has been thought that these buried plastics will remain forever on the coast. However, PS degrades at 30°C to generate SOs [26,27], indicating that these buried plastics receive light and heat from the sun and become sources of SOs during burial on beaches. SOs generated from PS became soluble in seawater and was detected in seawater and sand. SO is different from plastic (polymer) in that it has low molecular weight (molecular weight: 104/SM to 312/ST). It is considered that these chemicals easily metabolized in living organisms, and there is a concern that harmful effects on the marine ecosystem due to chemicals generated from the drifting plastics may be caused (Figure 2).

Invisible survey

GC/MS of SOs samples were collected for 15 years from 2000 to 2015. More than 200 locations in Japan, 1,441 of beach sand and 276 of seawater, totaling 1,717 samples. Analysis of each sample was performed within approximately two months after sampling. The sand on Iriomote island (Typically South side) and the seawater on Rebun

Table 2: Region (1 to 10) division and beach coast length in Japan.

Region	Area Division	Prefecture / Isolated Islands	Coastline length km
1	Hokkaido North	Hokkaido	558.2
2	Hokkaido South	Hokkaido	594.1
3	Japan Sea North	Aomori, Akita, Yamagata, Niigata, Toyama	336.0
4	Japan Sea West	Ishikawa, Fukui, Kyoto, Hyogo, Tottori, Shimane, Yamaguchi	588.0
5	Pacific Ocean North	Aomori, Iwate, Miyagi, Fukushima, Ibaragi	346.7
6	Pacific Ocean Central	Chiba, Tokyo, Kanagawa, Shizuoka, Aichi, Mie	334.0
7	Pacific Ocean South	Wakayama, Tokushima, Kochi, Ooita, Miyazaki	442.2
8	Setonaikai and Kyusyu East	Wakayama, Osaka, Hyogo, Okayama, Hiroshima, Yamaguchi, Fukuoka, Ooita, Ehime, Kagawa	406.2
9	Kyusyu West	Fukuoka, Saga, Kumamoto, Kagoshima	1118.2
10	Okinawa and Isolated islands	Rebun, Rishiri, Tobishima, Sado, Oki, Tsushima, Iki, Fukue, Hchijyo, Ogasawara/ Chichijima/Anishima, Okinawa, Ishigaki, Iriomote/ Sotobanarjijima /Uchibanarjijima	352.3
	Total		5034.0

island (Typically North side) were measured by Total Ion Monitor (TIM) -GC/MS, and the results are shown in Figure 3- (1) and (2). As shown in Figure 3, the chemicals detected from (1) and (2) are different from unknown (Un known: Un) in sand (1) and (2) water, but SOs (SM, SD₁, SD₂, ST) and phthalic acid ester (PAE) derived from polyvinyl chloride resin (PVC) plasticizer or polyethylene terephthalate (PET) (PAE: diethyl-phthalate, -dibutyl, -di-2-ethylhexyl, etc.) and bisphenol A (BPA) derived from polycarbonate or epoxy resin were detected (Figure 3).

Analysis accuracy: The GC/MS Total Scan Mode (TIM) measurement was analyzed, and the fragment ion m/z of the target chemical was determined. The quantitative analysis was performed by detecting selected ions from the molecular ions of each target chemicals (SIM, Selected ion monitoring) Monitoring channel was

Table 3: Mean values of SOs in sand and seawater of the coast collected from four major islands (Region 1 to 9) in Japan.

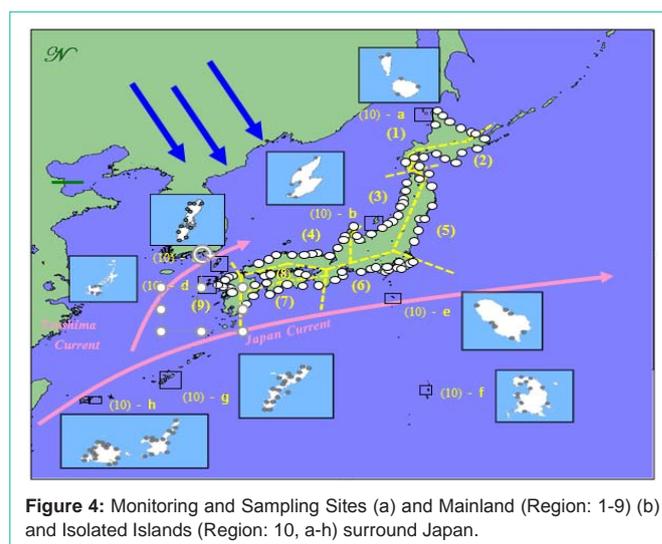
		Sand sample/ $\mu\text{g kg}^{-1}$						Seawater sample/ $\mu\text{g L}^{-1}$					
		Number of samples	SM	SD	ST	SO Total	Standard Deviaon	Number of samples	SM	SD	ST	SO Total	Standard Deviation
1	Hokkaido-North	100	4.2	16	89.1	105.1	13.1	16	0.15	0.35	1.58	2.08	2.63
2	Hokkaido-South	60	2.1	7.4	15.6	25.1	6.4	15	0.38	0.29	3.88	4.55	2.08
3	Japan Sea-North	100	2.8	35.2	408.1	446.1	13.6	20	0.42	0.5	7.02	7.95	16
4	Japan Sea-West	100	13.9	8.8	122.9	145.6	46.2	20	0.08	0.21	0.35	0.65	0.4
5	Pacific-North	60	1.2	3.3	9.6	14.1	15.8	17	0.09	0.04	1.2	1.33	7.69
6	Pacific-Central	320	82.1	48.2	189.7	320	5.24	80	0.22	0.44	2.47	3.13	6.65
7	Pacific-South	60	63.5	38.4	518.3	620.2	15	15	0.96	0.72	6.97	8.65	3.24
8	Setonaikai and Kyushu-East	40	84.1	60.4	664.8	809.3	11.6	10	0.49	0.52	3.15	4.16	3.89
9	Kyushu-West	160	150.8	149.2	692.3	992.3	46.9	14	0.75	0.31	2.76	3.82	5.58
	Total	1000	400.5	366.9	2710.4	3477.8		207	3.54	3.38	29.38	36.3	
	Average		44.5	40.8	301.2	386.4	19.3		0.39	0.38	3.26	4.03	5.4
	Ratio of SM:SD:ST		1	1	7				1	1	8		

set. Q (quantitative ion), m/z: 104, 154, 178, 196, 208, 312. I (qualitative ion), m/z: 78, 105, 117, 152, 193 ions are designated as monitor ions. A calibration curve was prepared by the internal standard method using the detected ion peak area ratio (I/Q) [28-31]. A 0.1 g 10 mL⁻¹ standard stock solution was prepared, and the target solution was prepared using a pipette and a volumetric flask. The calibration curve of each target substance was prepared using the SO standard solution. The linearity of the calibration curve was in the range of 0.01 μg to 10 $\mu\text{g g}^{-1}$ with a correlation coefficient (r), $r = 0.9996$ to 0.9999. The detection limit was determined as S/N = 2 and was 10 $\mu\text{g kg}^{-1}$. The Relative Standard Deviation (RSD) of the peak area of the internal standard and PT in each injection was within 2%. When 100 μg of BP and 100 mL⁻¹ of BP were added to the extracted DCM, the surrogate recovery was 90.3% to 97.8%, the average was 95.2% or more, and the RSD was within 7.3%.

Survey areas: Figure 4 shows the location of each survey areas surround Japan on the mainland (region 1-9, yellow character and dotted line) and the locate on of the isolated island (region-10, a to h: inside the blue frame). Considering the drifting process of drifting plastics, the currents around the Japan Sea (Kuroshio, Tsushima Oyashio, Liman- current,) and the seasonal wind are indicated by arrows. Table 2 shows the prefectures to which each region and the coast belong and the beach length. Table 2 Sea area and beach length, prefecture Figure 4 and Table 2, Region and Pref./Beach length.

In the management of coast line by the administration, Okinawa is applied to Kyushu west and the 9-region, but in this paper the Okinaw, Yaeyama and Sakishima islands are classified as region-10 (a to h): isolated island area.

SOs value in mainland: The mainland is 800 sand and 207 water samples, for a total of 1,007. The results were shown in Table 3. From Tables 3,4 the all means SOs value was 2.7 $\mu\text{g L}^{-1}$ for seawater and 488.7 $\mu\text{g kg}^{-1}$ for sand. Observing the SOs value of the sand in Table 2 and 3, region-9 with a long beach length is the highest SOs at 992.3 $\mu\text{g kg}^{-1}$. However, the SOs value per one kilometer of the beach is 2.0 for 8-region and five for region-9 in the all regions. This is suggesting SOs accumulation in closed seas (region-8). Japan has a 2,500 km north to

**Figure 4:** Monitoring and Sampling Sites (a) and Mainland (Region: 1-9) (b) and Isolated Islands (Region: 10, a-h) surround Japan.

south different latitude. The results of the sand SOs value in Table 3 tended to be high in the south and low in the north, and the effects of air and water temperature were recognized.

Since seawater is constantly mixed and diffused by waves, the SOs value is expected to be constantly changing. However, the measured standard deviation of seawater (SD: 3.4) is the deviation value of sand fixed on the coast (SD: 20.6) was 6 times smaller. The reason for this is unknown. The composition ratio of SOs (SM: SD: ST) was approximately 1: 1: 7 for sand and 1: 1: 8 for seawater. The SOs value of sand is three times higher in region-7, 8 and 9 than in the region-1, 2.

On the other hand, there was no significant difference in the SOs values of water in each region. On the mainland, it is expected that SOs will be supplied to the drifting coast from the inland area via the river, and it was considered that SOs was detected even at the point where drifting PS was low.

Table 2 and 3 the high SOs value per 1 km of beach length is,

Table 4: Mean Values of SOs in sand and seawater of the Coast Collected from 12 Isolated islands (Region 10).

Isolated Islands		Sand sample/ $\mu\text{g kg}^{-1}$						Seawater sample/ $\mu\text{g L}^{-1}$					
		Number of samples	SM	SD	ST	SO	Standard Deviation	Number of samples	SM	SD	ST	SO	Standard Deviation
Total	Total												
a	Rebun, Rishiri	32	58.4	47.5	195.3	301.2	5.57	10	0.19	0.25	2.44	2.88	0.18
b	Sado, Tobishima	24	6.3	15.8	173	195.1	16.64	6	0.01	0.26	0.79	1.06	1.24
c	Tsushima,Oki, Iki	64	111.2	155.8	1847	2114	2.1	6	0.18	0.2	2.03	2.41	7.17
d	Fukue	9	17.4	27.2	56.7	101.3	13.31	5	0.12	0.06	0.2	0.38	0.7
e	Hachijyo	16	11.1	13.5	323.6	348.2	8.76	5	0.12	0.06	0.17	0.35	0.13
f	Ogasawara/ Chichijima/Anishima	64	70.3	67	615.6	752.9	45.47	7	0.35	0.1	0.97	1.42	0.88
g	Okinawa	100	31.9	34	233.7	299.6	46.24	15	0.06	0.21	0.72	0.99	0.5
h	Ishigaki, Iriomote/ Sotobanarijima/ Uchibanarijima	132	52.5	46.8	516.5	615.8	42.84	15	0.12	0.35	0.67	1.14	0.54
	Total	441	359.1	407.6	3961.4	4728.1		69	1.15	1.49	7.99	10.63	
	Average		44.9	51	495.2	591			0.14	0.19	1	1.33	
	Ratio of SM:SD:ST		1	1	10		22.6		1	1	6		1.4

region-8: $2.0 \mu\text{g kg}^{-1}$, second, region-7: $1.4 \mu\text{g kg}^{-1}$, third, region-3: $1.3 \mu\text{g kg}^{-1}$ were detected, respectively. Table 3 SOs values (Mainland), Table 4 SOs values (Isolated islands)

SOs value in Isolated islands: Table 4 shows the results of SOs values on Isolated islands (Islands, region-10, a to h). 441 of sand and 69 samples of water for a total of 510.

The results of the sand SOs value in Table 4 tended to be high in the south (f: $752.9 \mu\text{g kg}^{-1}$, h: $615.8 \mu\text{g kg}^{-1}$) and low in the north (a, b: $301.2 \mu\text{g kg}^{-1}$), and the effects of air and water temperature were recognized same as mainland.

Most of Ogasawara/Chichijima and Anijima are national parks, the population is small, less than 3,000. Inland SO supplies to these coastal areas are considered to be negligible. However, the effect of drifting PS was recognized from the fact that the SOs value was less than the average of the isolated islands in water but 1.3 times large in sand.

Comparing three islands in region -10, h: Sakishima/Iriomote, Ishigaki with Okinawa, the SOs value of water is $1.14 \mu\text{g L}^{-1}$ and $0.99 \mu\text{g L}^{-1}$, respectively, lower than the average. However, the SOs value of sand was $300 \mu\text{g kg}^{-1}$ on Okinawa and $600 \mu\text{g kg}^{-1}$ on the Sakishima islands, suggesting the contribution of drifting PS over the supply of SOs from the land.

Conclusion

To date, no studies have been conducted on plastic degradation in the ocean owing to the misconception that plastic hardly degrades. The present study was conducted to clarify that drifting plastics do indeed break down. Not only does this happen through micro/nano-scale fragmentation, but invisible SOs chemicals are generated from debris PS. The compositions of PS degradation were found to be similar to that indicated by field analysis and on commercial product labels. PS was clearly shown to be unstable with the application of

heat, at temperatures attained in the ocean or in common use by people. Plastics are not metabolized subsequent to ingestion, since they are polymers. That being said, low molecular weight chemicals such as SOs, BPA possibly from polycarbonate or epoxy resin and PAE possibly from a plasticizer or polyethylene terephthalate are toxic and can be easily metabolized by biota. At present, macroscopic micro pollution can be observed visually due to plastic waste in the ocean. However, this study clearly demonstrates the creation of new chemical pollution, unseen to the human eye, from chemicals generated by plastic degradation in the ocean.

Thus, debris plastics in the ocean will certainly give rise to new sources of serious global contamination that will persist long into the future.

Acknowledgement

The authors gratefully acknowledge the following Atmosphere Ocean Research Institute, The University of Tokyo (AORI****): Prof. K.Kogure, Prof. A.Tsuda and Prof. H.Ogawa who provided valuable instruction.

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