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Letter

E-Waste Recycling Emits Large Quantities of Emerging Aromatic Amines and Organophosphites: A Poorly Recognized Source for Another Two Classes of Synthetic Antioxidants

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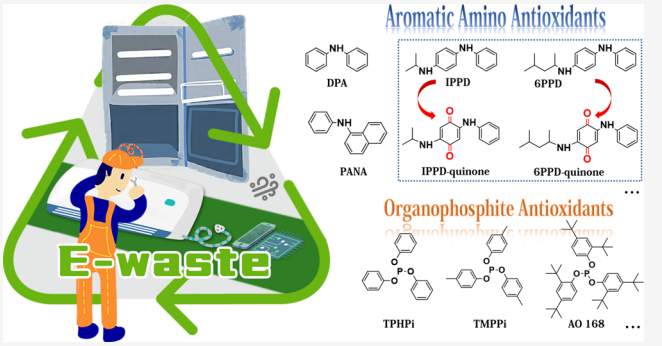
ABSTRACT: Our previous work demonstrated that massive emissions of hindered phenol antioxidants and sulfur-containing antioxidants from e-waste recycling; however, it remains unclear whether e-waste recycling also results in the emission of substantial quantities of amine antioxidants (AAs) and organophosphite antioxidants (OPAs), another two major classes of under-researched antioxidants. In this study, we continued to screen the previously studied e-waste dusts for a broad range of 21 AAs, two *p*-phenylenediamine-derived quinones, and 15 OPAs. All 21 AAs and 12 out of the 15 OPAs were detected in the samples, with the total concentrations ranging from 511 to 10,600 ng/g for AAs and from 155 to 33,200 ng/g for OPAs. Among the detected chemicals, nine were identified for the first time in the environment. More importantly, *N*-(1,3-dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine-quinone (6PPD-quinone), the causal toxicant of acute mortality in coho salmon, was pervasively detected with greater environmental abundance (median: 375 ng/g) than its parent chemical 6PPD (median: 113 ng/g), demonstrating that e-waste as another source of ubiquitous 6PPD-quinone in addition to tire rubber. Waste wires, cables, and electronic plastics were identified as the main sources for e-waste-derived AAs and OPAs. Our work highlights a large group of antioxidant chemicals, including their transformation products, as emerging e-waste pollutants that require more attention.



KEYWORDS: *amine antioxidants, 6PPD-quinone, organophosphite antioxidants, synthetic antioxidants, e-waste*

INTRODUCTION

Synthetic antioxidants are high-production-volume (HPV) industrial chemicals that have been widely used as additives in plastics, rubbers, wires, cables, and other polymer materials to prevent oxidative degradation of the products.[1−4] Because of the ever-evolving need for polymeric products, especially tire rubber, the global usage of synthetic antioxidants reached as high as 523,800 tons in 2018 and is expected to grow in the future.[5] On the basis of their chemical structures, commercial synthetic antioxidants are generally divided into four major classes: hindered phenolic antioxidants (HPAs), sulfur-containing antioxidants (SAs), aromatic amine antioxidants (AAs), and organophosphite antioxidants (OPAs).[6] Because of their broad use in large amounts globally, some synthetic antioxidants and selected oxidative transformation products have recently been identified as emerging contaminants pervasively present in various environmental matrices,[7−9] raising concerns on their ecological and health risks. Our previous research has discovered massive emission of HPAs and SAs from e-waste recycling,[10] offering new recognition for a significant environmental source; however, it is unclear whether e-waste recycling also results in the emissions of substantial quantities of AAs and OPAs, two other major classes of under-researched antioxidants.

Aromatic AAs are an important class in the primary antioxidant family and are generally subdivided into naphthylamines (NPAs), diphenylamines (DPAs), and *p*-phenylenediamines (PPDs). Recently, a quinone derivative of the tire rubber antioxidant *N*-(1,3-dimethylbutyl)-*N*′-phenyl-PPD (6PPD) formed by oxidative transformation, termed 6PPD-quinone, has attracted considerable international attention on PPDs because 6PPD-quinone was identified as the toxicant responsible for acute mortality in the Pacific Northwest coho salmon.[7] Subsequent studies have confirmed the ubiquitous occurrence of 6PPD and 6PPD-quinone in stormwater runoff, surface waters, air particles, and dust.[11−15] The same pathway

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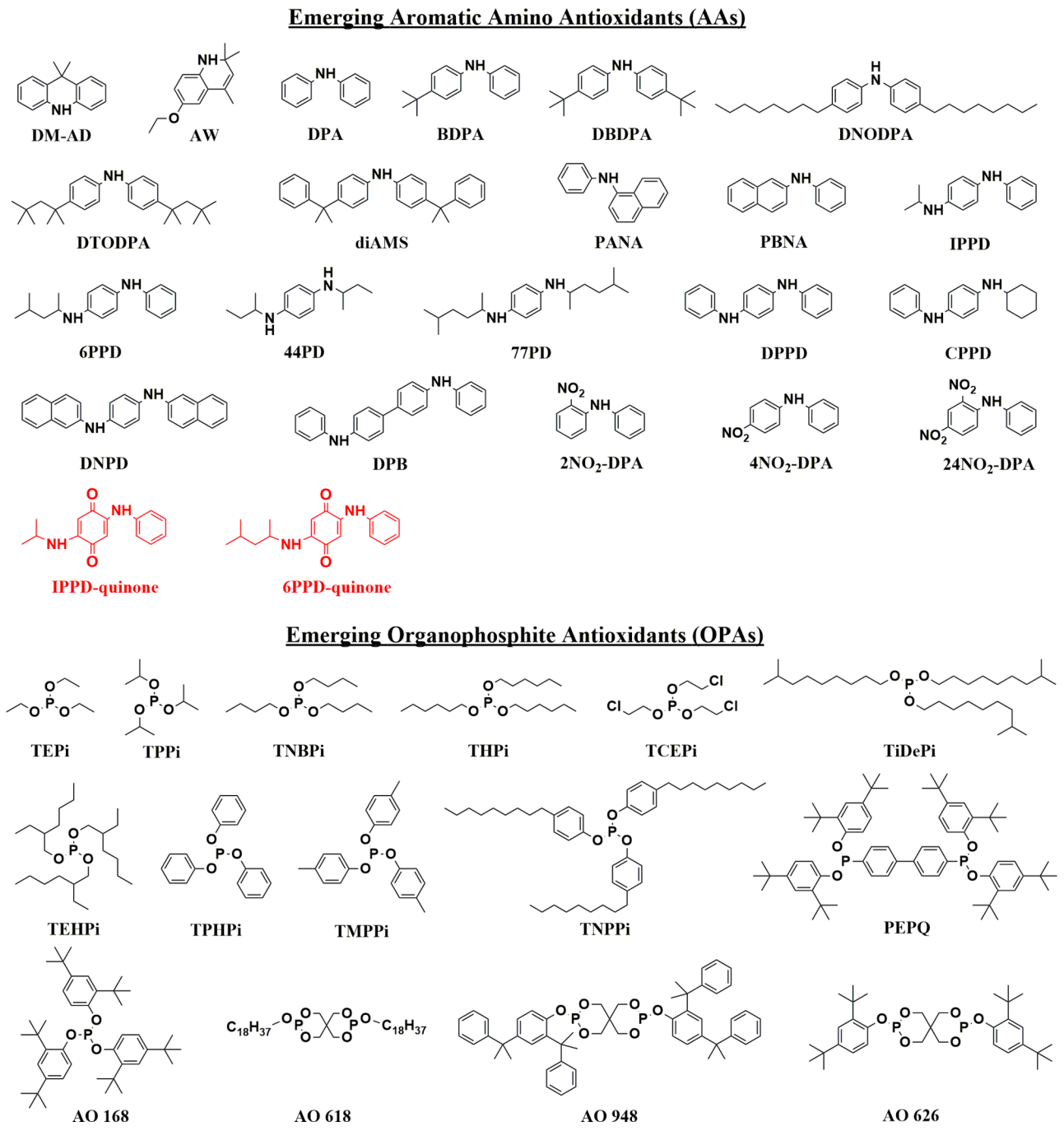

Figure 1. Chemical structures and abbreviations of a broad range of 21 emerging AAs, two PPD-derived quinones (IPPD-quinone and 6PPD-quinone, marked in red), and 15 emerging OPAs screened in this study.

may also produce quinones from other PPDs. A more recent study provided new evidence of multiple PPD-derived quinones in environmental media.[8] These selected PPDs and their derived quinones have also been verified to be toxic and pervasive in the environment.[16−20] In contrast to PPDs, NPAs and DPAs have rarely been investigated, and most have not yet entered the radar of toxicity or environmental studies.[21−26] Generally, environmental PPDs, NPAs, and DPAs are considered to be linked to tire rubber.[7,11,12,27] Comprehensive identifications of AAs, including PPDs, NPAs, and DPAs, as well as their significant sources other than tire rubber, are urgently needed to assess the overall risk.

OPAs are a class of common secondary antioxidants, which are extensively used in large quantities along with primary antioxidants such as AAs. A compelling example is tris(2,4-di*tert*-butylphenyl) phosphite (AO 168), with an annual production volume of ∼23,000 tons in the United States.[28] However, environmental information regarding OPAs is rather limited. The discovery of five OPAs in indoor dust has brought interest and attention to the source of contamination.[9] Three follow-up studies have demonstrated the existence of selected OPAs in film-mulching soil,[29] air particles,[30] and dust.[31] Although these studies focused on only a few OPAs, all results suggested that OPAs represent an important indirect source of environmental organophosphate esters (OPEs), the OPA

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Table 1. Descriptive Statistics of Concentrations (ng/g) of 21 Emerging AAs, Two PPD-Derived Quinones, and 15 Emerging OPAs Detected in 45 E-Waste Dust Samples from Diverse E-Waste Recycling Workshops

Antioxidants	CAS RN	Molecular formula	DF[a] (%)	GM[b]	Median	Mean	Range	AP[c] (%)
Emerging Aromatic Amine Antioxidants (AAs)								
DM-AD	6267-02-3	$C_{15}H_{15}N$	60	19.3	29.1	83.1	<MQL to 896	1.9
AW	91-53-2	$C_{14}H_{19}NO$	11	<MQL	<MQL	<MQL	<MQL to 10.3	0.0
DPA	122-39-4	$C_{12}H_{11}N$	100	190	197	272	22.9 to 1.85×10^3	8.3
BDPA	4496-49-5	$C_{16}H_{19}N$	100	20.5	22.0	28.9	2.01 to 120	1.0
DBDPA	4627-22-9	$C_{20}H_{27}N$	100	39.0	35.4	73.4	3.00 to 456	2.2
DNODPA/DTODPA	101-67-7/15721-78-5	$C_{28}H_{43}N$	100	50.9	39.2	151	5.40 to 1.17×10^3	4.0
diAMS	10081-67-1	$C_{30}H_{31}N$	100	173	124	270	28.2 to 1.30×10^3	8.1
PANA/PBNA	90-30-2/135-88-6	$C_{16}H_{13}N$	100	203	172	499	19.1 to 5.50×10^3	12.2
IPPD	101-72-4	$C_{15}H_{18}N_2$	100	373	424	776	18.1 to 6.68×10^3	19.4
6PPD	793-24-8	$C_{18}H_{24}N_2$	100	126	113	194	13.8 to 1.02×10^3	6.7
44PD	101-96-2	$C_{14}H_{24}N_2$	13	<MQL	<MQL	<MQL	<MQL to 12.8	0.0
77PD	3081-14-9	$C_{20}H_{36}N_2$	36	3.14	<MQL	19.1	<MQL to 243	0.5
DPPD	74-31-7	$C_{18}H_{16}N_2$	53	7.53	16.0	38.2	<MQL to 628	0.9
CPPD	101-87-1	$C_{18}H_{22}N_2$	40	1.02	<MQL	3.47	<MQL to 19.2	0.1
DNPD	93-46-9	$C_{26}H_{20}N_2$	49	31.8	<MQL	178	<MQL to 1.79×10^3	5.5
DPB	531-91-9	$C_{24}H_{20}N_2$	64	1.53	2.27	4.87	<MQL to 45.6	0.1
$2NO_2$-DPA	119-75-5	$C_{12}H_{10}N_2O_2$	100	144	168	314	12.2 to 1.50×10^3	11.2
$4NO_2$-DPA	836-30-6	$C_{12}H_{10}N_2O_2$	100	243	262	492	29.2 to 3.36×10^3	16.2
$24NO_2$-DPA	961-68-2	$C_{12}H_9N_3O_4$	100	37.1	39.6	49.6	2.64 to 196	1.7
$\sum_{21}$AAs	–	–		2.86×10^3	2.98×10^3	3.45×10^3	511 to 1.06×10^4	100
IPPD-quinone	–	$C_{15}H_{16}N_2O_2$	71	250	363	817	<MQL to 6.59×10^3	–
6PPD-quinone	–	$C_{18}H_{22}N_2O_2$	100	399	375	572	87.1 to 2.85×10^3	–
Emerging Organophosphite Antioxidants (OPAs)								
TEPi	122-52-1	$C_6H_{15}O_3P$	11	<MQL	<MQL	5.50	<MQL to 69.2	0.4
TPPi	116-17-6	$C_9H_{21}O_3P$	13	<MQL	<MQL	45.8	<MQL to 490	2.7
TNBPi	102-85-2	$C_{12}H_{27}O_3P$	67	11.6	13.5	20.7	<MQL to 91.8	2.5
THPi	6095-42-7	$C_{18}H_{39}O_3P$	13	<MQL	<MQL	140	<MQL to 1.95×10^3	5.5
TCEPi	140-08-9	$C_6H_{12}Cl_3O_3P$	18	<MQL	<MQL	131	<MQL to 1.77×10^3	6.0
TiDePi	25448-25-3	$C_{30}H_{63}O_3P$	0	<MQL	<MQL	<MQL	<MQL	0.0
TEHPi	301-13-3	$C_{24}H_{51}O_3P$	7	<MQL	<MQL	145	<MQL to 3.64×10^3	4.5
TPHPi	101-02-0	$C_{18}H_{15}O_3P$	40	1.29	<MQL	6.04	<MQL to 43.2	0.5
TMPPi	620-42-8	$C_{21}H_{21}O_3P$	47	1.35	<MQL	4.47	<MQL to 102	1.1
TNPPi	3050-88-2	$C_{45}H_{69}O_3P$	44	3.45	<MQL	24.5	<MQL to 556	1.5
PEPQ	38613-77-3	$C_{68}H_{92}O_4P_2$	0	<MQL	<MQL	<MQL	<MQL	0.0
AO 168	31570-04-4	$C_{42}H_{63}O_3P$	100	893	918	1.80×10^3	97.0 to 3.30×10^4	70.0
AO 618	3806-34-6	$C_{41}H_{82}O_6P_2$	0	<MQL	<MQL	<MQL	<MQL	0.0
AO 948	154862-43-8	$C_{53}H_{58}O_6P_2$	7	<MQL	<MQL	93.7	<MQL to 2.58×10^3	3.5
AO 626	26741-53-7	$C_{33}H_{50}O_6P_2$	13	<MQL	<MQL	34.6	<MQL to 1.11×10^3	1.7
$\sum_{15}$OPAs	–	–		1.38×10^3	1.55×10^3	2.45×10^3	155 to 3.32×10^4	100

[a]Detection frequency. [b]Geometric mean. [c]Average proportion in each group.

oxidation products. Therefore, the complete identification of OPAs together with potential emission sources is also important for understanding their overall risk.

E-wastes, such as wires, cables, and electronic plastics, are significant waste streams and have been demonstrated to be a significant source of HPAs and SAs by our research group.[10] To address the knowledge gaps stated above, this study continues from our previous work[10] and extends to screen for AAs and OPAs that are possibly present in high abundances but are less of a concern. A broad suite of 23 AAs (including two PPD-derived quinones) and a complete suite of 15 OPAs were included in our dedicated target screening. The primary aim is to shape a complete picture of the four major classes of synthetic antioxidants emitted by e-waste recycling through a full screening and shed new light on poorly recognized e-waste sources. Our findings will greatly expand the existing knowledge of environmental synthetic antioxidants and stimulate further investigations on their ecological and health risks.

MATERIALS AND METHODS

Standards and Reagents. A broad suite of 21 emerging aromatic AAs, including 11 DPAs (DM-AD, DPA, BDPA, DBDPA, DNODPA, DTODPA, diAMS, DPB, $2NO_2$-DPA, $4NO_2$-DPA, and $24NO_2$-DPA), seven PPDs (IPPD, 6PPD, 44PD, 77PD, DPPD, CPPD, and DNPD), two NPAs (PANA and PBNA), and one quinolone (AW), and a complete suite of 15 emerging OPAs, namely, TEPi, TPPi, TNBPi, THPi, TCEPi, TiDePi, TEHPi, TPHPi, TMPPi, TNPPi, PEPQ, AO 168, AO 618, AO 948, and AO 626, were included for "novel" antioxidant target screening in this study, which were purchased from Tokyo Chemical Industry (Tokyo, Japan),

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AccuStandard (New Haven, CT), and J&K Scientific Ltd. (Beijing, China), with a purity of greater than 98%. Two PPD-derived quinones, named IPPD-quinone and 6PPD-quinone, were obtained from Dr. Ehrenstorfer (Augsburg, Germany), with a purity of 97.8%. The chemical structures of all 38 target compounds are shown in Figure 1, and their full names, CAS numbers, and key physicochemical properties are summarized in Table S1. These available standards have covered almost all AAs and OPAs that are commonly used in industrial products worldwide. Six isotope-labeled standards, namely, diphenylamine-d_{10} (DPA-d_{10}), $^{13}C_6$-6PPD-quinone, $^{13}C_{12}$-benzophenone-3 ($^{13}C_{12}$−BP-3), tributyl phosphate-d_{27} (TNBP-d_{27}), tris(2-chloroethyl) phosphate-d_{12} (TCEP-d_{12}), triphenyl phosphate-d_{15} (TPHP-d_{15}), and tricresyl phosphate-d_{21} (TMPP-d_{21}), were chose as surrogate standards, supplied by Toronto Research Chemicals (Burlington, Canada) and Cambridge Isotope Laboratories (Andover, USA).

Field Sample Collection. E-waste dust samples were collected from 45 e-waste recycling workshops in a mega e-waste recycling industrial park in South China during August 2020. One composited sample was collected from each e-waste recycling workshop. The 45 sampled e-waste recycling workshops include 12 wire and cable dismantling workshops and 12 electronic plastic processing workshops, while the others are the general e-waste recycling workshops that dispose of common e-wastes, such as waste televisions, computers, refrigerators, air conditioners, and washing machines. Detailed sampling information can be found in our previous work.[10]

Sample Preparation and Instrumental Analysis. The sample preparation procedures were based upon our previously developed method[10] with moderate modifications. The target screening and simultaneous quantitative analysis of 21 AAs, two PPD-derived quinones, and 15 OPAs were developed by an ExionLC AC ultrafast liquid chromatography mass coupled to a Triple Quad 5500 mass spectrometer (LC-MS/MS, AB Sciex, Framingham, MA, USA). Details on the sample preparation and instrumental analysis are given in the Supporting Information (SI). Ion transitions and optimized parameters for all target compounds and surrogate standards are summarized in Tables S2. Total and individual chromatograms of the 38 target compounds are shown in Figures S1 and S2, respectively.

Quality Assurance and Quality Control (QA/QC). A series of strict QA/QC measures were performed throughout the whole analytical process to ensure accurate identification and quantification, including the analysis of procedural blanks, field blanks, matrix spike recoveries, and surrogate standard recoveries. The method detection limit (MDL) and method quantification limit (MQL) were defined as an analyte concentration with a signal-to-noise ratio of 3 and 10, respectively, for all target antioxidants, with the exception of AO 168, whose MDL and MQL were calculated as the average blank plus 3 and 10 times the standard deviation, respectively. The MDLs and MQLs varied in the ranges of 0.038−13 and 0.13−43 ng/g, respectively (Table S3). Details of the QA/QC results and data analysis are described in the SI.

RESULTS AND DISCUSSION

Comprehensive Identification of Emerging AAs, Including Highly Abundant PPD-Derived Quinones, in E-Waste Dust. Descriptive statistics of the concentrations of 21 emerging AAs and two PPD-quinones in e-waste dust samples are shown in Table 1. DNODPA and DTODPA are structural isomers and could not be separated using the XBridge BEH C8 column; thus, they were quantified together. Similarly, PANA and PBNA are structural isomers that were also quantified together. All 21 AAs and the two PPD-quinones were detected in the samples, demonstrating their broad existence. A considerable portion of the detected AAs, including DM-AD, AW, 44PD, 77PD, DPPD, CPPD, DNPD, 24NO_2-DPA, IPPD-quinone, and 6PPD-quinone, were reported for the first time in e-waste dust, and some, such as AW and 44PD, were newly identified in the environment. A total of 12 of the 23 target aromatic amines exhibited a detection frequency (DF) of 100%, indicating that they are a class of particularly important yet inadequately recognized antioxidants prevailing in e-waste recycling work environments. The total concentration of the 21 AAs ($\sum_{21}$AAs) in e-waste dust ranged from 511 to 1.06×10^4 ng/g, with a median of 2.98×10^3 ng/g. The median total level of AAs was substantially lower than that of our previously reported HPAs[10] but significantly higher than that of SAs ($p < 0.05$).[10] These new data highlight the abundant, pervasive occurrences of a large number of AAs in e-waste recycling workshops and demonstrate broad emission of AAs from e-waste recycling.

For individual AAs detected in South China e-waste dust, their respective concentrations and DFs were substantially higher compared to some previously identified AAs in house dust and the general e-waste dust,[15,21,32] suggesting that AAs could be significantly emitted from certain specific e-waste sources. Among the AAs with a DF of 100%, DPA, diAMS, PANA/PBNA, IPPD, and 6PPD were identified as the predominant, abundant components, with their median levels exceeding 100 ng/g. These six predominant AAs accounted for an average contribution of 54.7% to the $\sum_{21}$AAs. Although BDPA, DBDPA, and DNODPA/DTODPA were detected in all the samples, they showed relatively low median levels (22.0−39.2 ng/g), indicating that their usage in electronic products (e-products) is frequent but not substantial. DM-AD, 77PD, DPPD, CPPD, DNPD, and DPB were detected in 36%−64% of the samples with relatively lower levels. AW and 44PD, as newly identified AAs, were detected in a few samples only, implying their minor use in e-products. Interestingly, 2NO_2-DPA, 4NO_2-DPA, and 24NO_2-DPA are generally considered to be the nitration transformation products of DPA;[21,32,33] all were ubiquitously detected with high concentrations comparable to that of DPA. Significant correlations were found among three NO_2-DPAs and between NO_2-DPAs and DPA (Table S4; $r = 0.339$−0.864, $p < 0.05$). More importantly, unexpectedly high concentrations of IPPD- and 6PPD-quinones were pervasively found in e-waste dust, with medians of 363 and 375 ng/g, respectively, similar to or even higher than those of their parents IPPD and 6PPD. Significant correlations between PPD-quinones and their respective parent PPDs were observed (Figure S3; $r^2 = 0.69$ and 0.43, $p < 0.01$), indicating significant indoor transformation of PPDs into PPD-quinones. The 6PPD-quinone has been confirmed as a causal toxicant to multiple aquatic species.[7,16,17] The contribution of e-waste- or plastic-produced 6PPD-quinone to the aquatic environment and humans may be emerging issues worthy of concern. To the best of our knowledge, this is the first comprehensive identification of a wide range of AAs, including crucial transformation products, associated with e-waste recycling.

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Comprehensive Identification of Emerging OPAs in E-Waste Dust. A total of 12 of the 15 target OPAs were detected in e-waste dust. Among the 12 detected OPAs, seven OPAs (TEPi, TPPi, TNBPi, THPi, TEHPi, TMPPi, and AO 948) were identified for the first time in the environment. AO 168 was extensively detected in all e-waste dust samples and identified as the most abundant OPA, with the median and highest levels reaching 918 and 3.30×10^4 ng/g, respectively, which is 2 orders of magnitude greater than its previously reported levels in indoor dust.[9] AO 168 is an HPV chemical recorded in the US EPA CDR database,[28] which has been reported to be detected at very high concentrations in commercial mulch film[29] and face masks.[34] Our finding of highly abundant AO 168 in e-waste dust implies that it is extensively used in substantial amounts across diverse e-products, such as wires and cables. Interestingly, AO 168 was rarely or not detected in outdoor matrices, such as air fine particles and film-mulching soil.[29,30] Considering the similarity in molecular structures of OPAs and OPEs, evidenced partly by previous studies, OPAs may readily undergo environmental oxidative transformation to generate OPEs, representing an important indirect source of environmental OPEs that had been previously overlooked.[9,29−31] This raises another emerging issue worthy of further concern.

The second abundant OPA was found to be TNBPi, which was detected in 67% of the e-waste samples, with a median of 13.5 ng/g, substantially lower than that of AO 168. All the remaining OPAs, except TiDePi, PEPQ, and AO 618, could be detected but showed low DFs (< 50%). Consistent with previous studies on selected OPAs,[9,29−31] the compounds TCEPi, TPHPi, TEHPi, TiDePi, TNPPi, and AO 626 were difficult to find in other environmental matrices or were positively detected but with low levels and DFs. According to the US EPA CDR database,[28] some OPAs, such as TPHPi and TNPPi, are also HPV chemicals similar to AO 168. Their low concentrations and DFs imply that they more readily undergo oxidative transformation to form OPEs. The total concentration of the 15 OPAs ($\sum_{15}$OPAs) in e-waste dust ranged from 155 to 3.32×10^4 ng/g (median: 1.55×10^3 ng/g), indicating they are another emerging class of e-waste pollutants that cannot be ignored and highlighting the urgent need for future research into their environmental fate and risks. This is the first comprehensive identification of a wide range of OPAs associated with e-waste recycling.

Source Tracking and Composition Profile of Synthetic Antioxidants Emitted by E-Waste. Most synthetic antioxidants are semivolatile organic compounds. As additive chemicals, they are well likely to leach from various waste e-products during their dismantling processes and tend to partition into different compartments, through direct dispersion in indoor air, adsorption, and/or transfer to dust. Significant positive relationships were observed between most of the commonly used AAs, especially between the pairs of DPAs and NPAs, identified in the e-waste dust (Table S4; r = 0.301−0.911, $p < 0.05$), indicating their similar commercial applications and common emission sources/pathways. To gain insight into specific emission sources of AAs and OPAs during e-waste recycling, we further compared the concentrations among the three types of e-waste dusts collected from various e-waste recycling workshops. As shown in Figure 2A, dust concentrations of $\sum_{21}$AAs and $\sum_{15}$OPAs from workshops processing wires, cables, and electronic plastics are significantly greater than those from workshops processing general e-wastes,

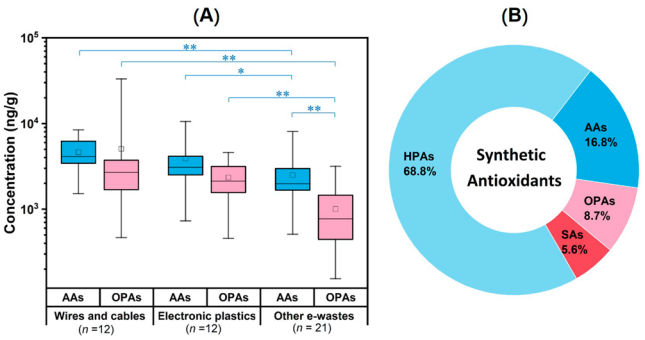

Figure 2. (A) Variations in concentrations of AAs and OPAs detected in e-waste dust from different types of e-waste recycling workshops. The boxes represent the 25th, 50th, and 75th percentiles. The squares within the boxes indicate the mean values. The whiskers represent the maximum and minimum values. The one and two asterisks denote significant differences in concentrations at the $p < 0.05$ and 0.01 levels, respectively. (B) Relative abundances of the four major classes of synthetic antioxidants, namely, AAs, OPAs, HPAs, and SAs, distributed in e-waste dust. Data of HPAs and SAs are from our previously published study.[10]

such as televisions and computers ($p < 0.05$). The dust pollution patterns of AAs and OPAs were similar to that of HPAs that we have previously reported in the same samples.[10] This provided clear evidence of wires, cables, and electronic plastics being more significant emission sources for synthetic antioxidants compared to the general e-wastes. Generally, cables and wires are wrapped with rubber or plastics as common insulating materials. Direct determinations of these chemicals in diverse insulating materials and electronic plastics will provide insights into the sources. A principal component analysis (PCA) was used to determine which individual AAs and OPAs were driving the differences in the composition distribution among the sampling sites (Figure S4). The PCA results showed that DBDPA, diAMS, and PANA/PBNA were more abundant in samples from wire and cable recycling workshops, while IPPD, $4NO_2$-DPA, and $2NO_2$-DPA had higher relative abundance in samples from electronic plastic recycling workshops. Samples from other e-waste recycling workshops did not form a distinct cluster on the biplot, indicating that their composition profiles were similar to the average pattern across the e-waste dusts.

Further, we discovered the composition profile and relative abundances of the four major classes of synthetic antioxidants emitted by e-waste recycling by integrating our previously reported data on HPAs and SAs into an overall analysis.[10] As shown in Figure 2B, HPAs were the most abundant antioxidants emitted by e-waste recycling, accounting for 68.8% of all emitted antioxidants, followed by AAs (16.8%), OPAs (8.7%), and SAs (5.6%). This might be consistent with their respective usage amounts in the e-product manufacturing industry; however, no related information is available at present. To date, our studies have identified and demonstrated a vast family of synthetic antioxidants coemitted by e-waste recycling, which showed substantially higher joint concentrations than the well-known e-waste pollutants, such as polychlorinated biphenyls and OPEs,[35−37] and require more attention.

Future Perspectives. Our previous study demonstrated massive emissions of potentially hazardous HPAs and SAs from e-waste recycling.[10] Together with the current study on

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AAs and OPAs, we have comprehensively identified and confirmed all four major classes of synthetic antioxidants as a large group of emerging e-waste pollutants pervasive in e-waste recycling regions and gained insight into their specific sources. More importantly, in addition to these parent chemicals, we have newly discovered the environmental ubiquity of e-waste-derived 6PPD-quinone and IPPD-quinone, with significant environmental abundances. Although the strong acute toxicity of 6PPD-quinone to multiple aquatic species, particularly coho salmon, has been verified,[7,38] the biotoxicity of other PPD-quinones to aquatic and terrestrial ecosystems remains unclear. Health risks due to human exposure, especially in occupational workers, to these emerging chemicals still remain unknown. Therefore, deeper investigations into their environmental transformations, fates, and toxicities are urgently necessary. Considering the limited attention paid to environmental transformation within existing contaminant assessment frameworks, our work highlights the urgent need to include transformation products in the development of regulations for synthetic antioxidant chemicals of emerging concern.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.2c00366.

Basic information on 21 AAs, two PPD-quinones, and 15 OPAs (Table S1), optimized ESI (+)-MS/MS parameters for the 38 target compounds (Table S2), QA/QC data (Table S3), Spearman's correlation analysis (Table S4), total and individual chromatograms (Figures S1 and S2), correlations between two PPD-quinones and their respective parents (Figure S3), and principal component analysis (Figure S4) (PDF)

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Notes

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