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Amino accelerators and antioxidants in sediments from the Dong Nai River System, Vietnam: Distribution and influential factors

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ABSTRACT

Amino accelerators and antioxidants (AAL/Os) have become a suite of contaminants of emerging concern recently due to the accumulating evidence for their environmental occurrence and associated toxic potential. Nevertheless, data on sedimentary deposition of AAL/Os has remained scarce, particularly for regions beyond the North America. In the present study, we elucidated spatial distribution of fifteen AAL/Os and five AAO transformation products (AAOTPs) in seventy-seven sediments from the Dong Nai River System (DNRS), Vietnam. Total concentrations of AAL/Os (∑AAL/Os) ranged from 0.377 to 51.4 ng/g (median: 5.01 ng/g). 1,3-Diphenylguanidine and 4,4′-*bis*(1,1-dimethylbenzyl) diphenylamine were the two most prevalent congeners, both with detection frequencies >80%. Additionally, AAOTPs were quantifiable in 79% of the DNRS sediments with a median ∑AAOTPs at 2.19 ng/g, dominated by *N, N*′-diphenylbenzidine and 2-nitrodiphenylamine. Higher sediment-associated levels of AAL/Os and AAOTPs were spotted in downstream and the primary tributary of the DNRS compared to the upstream, implying their cumulative sedimentation towards the estuarine region. The distribution patterns of AAL/Os and AAOTPs across individual transects also demonstrated the influence of human activities (e.g., urbanization and agriculture), hydrodynamics, and decontamination by mangrove reserves. Meanwhile, characteristics of sediments, i.e., total organic carbon (TOC) content and grain sizes, exhibited significant correlations with the burdens of these compounds, indicating their preferential partitioning into the fine and TOC-rich matter. This research sheds light on environmental behavior of AAL/Os and AAOTPs beneath Asian aquatic system, and highlights the need for further evaluation of their impacts on the wildlife and public health.

1. Introduction

Amino accelerators and antioxidants (AAL/Os) are two classes of synthetic aniline-based chemicals massively used in numerous consumer products, particularly latex, natural and synthetic rubber products, like tires, cables, and shoes (Sieira et al., 2020; WuVenier, 2022; Zhang et al., 2021). The latter can inhibit the initiation and growth of free radical chain reactions by providing the active hydrogen on their amino groups and trapping peroxy species, to prevent oxidative aging, corrosion, and explosion of the products to which they are added (Drzyzga, 2003; Lu et al., 2017). While AALs, such as 1,3-diphenylguanidine (DPG) and 1, 3-di-*o*-tolylguanidine (DTG), have been widely utilized to catalyze the cross-linking of rubber with sulfur in the vulcanization process (Johannessen et al., 2021a; Sieira et al., 2020). Due to the large-scale manufacturing and use, several AAL/Os have been listed as high yield compounds. For example, the latest annual production volumes of *N*-(1, 3-dimethylbutyl)-*N*′-phenyl-*p*-phenylenediamine (6 PPD) were 22700-45400 and 10000-100000 tons in the United States and Europe,

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respectively, and the corresponding yields for DPG have reached 454–9070 and 1000–10000 tons (ECHA, 2022; USEPA, 2022). Although official statistics on the usage of AAL/Os in Asia have remained unavailable, this region has experienced a rapid expansion in relevant industries, e.g., automotive and rubber, likely constituting a significant portion of global AAL/O application.

Mounting attention has been paid to AAL/Os in recent years since an increasing number of studies confirmed their environmental persistence, bioaccumulative potential, and toxicity. A myriad of AAL/Os and amino antioxidant transformation products (AAOTPs), e.g., 2-nitrodiphenylamine (2-NO_2-DPA), 4-nitrodiphenylamine (4-NO_2-DPA), and *N*-(1,3-dimethylbutyl)-*N*′-phenyl-p-phenylenediamine quinone (6 PPD-Q), have been widely detected in various environmental matrices, including atmospheric particles, surface water, wastewater, sewage sludge, sediments, soil, dust, and biota (Cao et al., 2022; Challis et al., 2021; Lu et al., 2018; Tan et al., 2021; Wang et al., 2022; Zhang et al., 2021). Moreover, adverse effects of AAL/Os and AAOTPs [AAL/O(TP)s] on wildlife, particularly aquatic organisms, have been documented. Chibwe et al. (2022) exposed fathead minnows (*Pimephales promelas*) to leachates of tire-wear particles with DPG levels up to 13000 ng/L, and observed that such exposure may link to severe deformities (e.g., cardiac edemas, blunted face, and malformed jaws), shortened body size, lower heart rates and hatching success, as well as lack of body pigments. Sediment-associated diphenylamine (DPA) and *N*-phenylnaphthyl-1--amine (PANA) could impair reproduction and development of juvenile sludge worms (*Tubifex tubifex, Lampsilis siliquoidea,* and *Pimephales promelas*) (Prosser et al., 2017a, 2017b, 2017c). 6 PPD could incur acute and chronic toxicity to freshwater organisms (Peng et al., 2022; Tian et al., 2021), while its oxidation product, 6 PPD-Q, was reported to cause mortality to coho salmon (*Oncorhynchus kisutch*) even at the ng/L levels (Tian et al., 2021, 2022).

The Dong Nai River System (DNRS) lies in the Can Gio district of Ho Chi Minh City, Vietnam (106°38′-107°11′E and 10°20′-19°50′N), which receives discharge water from a catchment area of roughly 38600 km^2 (Nguyen et al., 2019). As the longest Vietnamese river, the DNRS is comprised of two large streams (the Soai Rapp River and the Long Tau River) and 2 minor tributaries (the Vam Co River and the Thi Vai River), supplying drinking water, navigation, fisheries, and hydroelectric power to more than 19 million people (Gugliotta et al., 2020; Ma et al., 2022; Truong and NguyenKondoh, 2018). Consequently, studies have been conducted to explore build-ups of legacy and emerging contaminants in this watershed, including organochlorine pesticides, per- and polyfluoroalkyl substances (PFAS), and organophosphate esters (OPEs) (Lam et al., 2017; Ma et al., 2022; Nguyen et al., 2019).

Given the widespread occurrence and proven toxicity of AAL/Os, as well as the paucity of information on their environmental profiles for regions outside the North America, here we examined fifteen AAL/Os and 5 AAOTPs in seventy-seven sediment samples collected from the DNRS and one of its tributaries, Vam Co River. The objectives of this study were to (1) determine concentrations and composition of AAL/Os and AAOTPs in the DNRS sediments; (2) unveil the spatial patterns and address influencing factors; (3) investigate the impacts of properties of sediments on accumulation of these compounds. Our results constitute an essential contribution to tackling the puzzle of AAL/O distribution in less-studied regions.

2. Material and method

2.1. Chemicals and reagents

Authentic standards of two AALs, i.e., DPG and DTG, thirteen AAOs, namely DPA, PANA, *N*-phenylnaphthyl-2-amine (PBNA), 4-*tert*-butyl diphenylamine (BDPA), *N*-isopropyl-*N*′-phenyl-*p*-phenylenediamine (IPPD), *N, N*′-diphenyl-*p*-phenylenediamine (DPPD), N_1-cyclohexyl-N_4-phenyl-benzene-1,4-diamine (CPPD), 6 PPD, 4,4′-di-*tert*-butyl diphenylamine (DBDPA), 4-octyl diphenylamine (ODPA), *N, N*′-di-2-naphthyl-*p*-phenylenediamine (DNPA), 4,4′-dioctyl diphenylamine (DODPA), and 4,4′-bis(1,1-dimethylbenzyl) diphenylamine (diAMS), five AAOTPs, i.e., 2-NO_2-DPA, 4-NO_2-DPA, 4,4′-dinitrodiphenylamine (4,4′–NO_2–DPA), 6 PPD-Q, and *N,N*′-diphenylbenzidine (DPB), as well as those of isotopically-labelled compounds adopted as surrogate (d_{10}-DPA, $^{13}C_6$-PBNA, d_{10}-DPG, and d_5-6 PPD-Q) and internal standards (d_6-DPA) were purchased from AccuStandard (New Haven, CT), Toronto Research Chemicals (Ontario, Canada), Tokyo Chemical Industry (Shanghai, China), and CATO Research Chemicals (Guangzhou, China) (see Table S1 for the detailed information). The purity of all standards was >95%. Our analytes have been reported to occur in various environmental matrixes, and their standards have become commercially available. The sodium sulfate and solvents at high-performance liquid chromatography (HPLC) grade or higher were obtained from Anpel Laboratory Technologies (Shanghai, China). The solid phase extraction (SPE) cartridges packed with C_{18}-octadecyl silane (ODS, 200 mg, 3 mL) and centrifugal filters (nylon membrane, 0.2 μm) were from Agilent (Santa Clara, CA) and Thermo Fisher Scientific (Waltham, MA), respectively.

2.2. Sample collection

In May 2018 (wet season), seventy-seven sediment samples were collected from the downstream (N = 20; sites: DS1 – DS19), midstream (N = 12; MS1 – MS12), and upstream (N = 18; US1 – US17) of the Dong Nai River, as well as the primary (N = 20; PT1 – PT20) and secondary tributaries (N = 7; ST1 – ST7) along the Vam Co River. Our sampling sites were randomly chosen and equally distributed (approximately 4 km between adjacent two locations) along with the final 90 km of mainstream and the final 50 km of associated tributaries, well covering the entire estuarine aera (Gugliotta et al., 2020). Six vertical transects (width: 0.46–1.71 km), consisting of 6–12 evenly distributed grabbing sites individually, were gathered to depict the gradient of chemical levels between banks (see Fig. 1; detailed sample information is provided in Table S2). The sampling procedure was described elsewhere (Ma et al., 2022). In brief, the sediments were collated using a KS grab sampler (15 cm × 15 cm; 2.7 L; Rigo Corp., Tokyo, Japan) and transported to analytical laboratories immediately. A quarter of each sample was stored at 4 °C for grain size measurement, while the remaining sediment was freeze-dried, homogenized, and sieved prior to determination of the content of total organic carbon (TOC) as well as AAL/Os and AAOTPs.

2.3. Sample analysis

The concentrations of AAL/Os and AAOTPs were determined followed our previously established analytical methodology with minor modification (Wu and VenierHites, 2020). Approximately 200 mg aliquots of sediment samples were spiked with 10 ng each of surrogate standards and extracted with 3 mL of 1:1 methanol/acetonitrile thrice. Each extraction step involved 30-min sonication followed by centrifuge at 2920×*g* for 10 min. The supernatants were combined and reduced to 1 mL with nitrogen blowdown, and the resulting extract was cleaned-up by passing through the ODS-sorbent SPE column, which was pre-conditioned with 10 mL of methanol. After the sample was loaded, our analytes were eluted using 6 mL of methanol. The eluant was concentrated under nitrogen till 200 μL, filtered using a centrifugal filter, and spiked with internal standard (i.e., 10 ng d_6-DPA) prior to instrumental analysis.

All target compounds were analyzed by ultra-high performance liquid chromatography interfaced with a triple quadrupole mass spectrometer (Acquity UPLC – Xevo TQ-XS MS; Waters, Milford, MA), operated under the positive electrospray ionization mode (ESI^+). An Acquity BEH C_{18} column (50 mm × 2.1 mm × 1.7 μm; Waters, Milford, MA) was used for separation of analytes. The mobile phases were 0.1% formic acid in water (A) acetonitrile (B). The initial phase B% was 10%

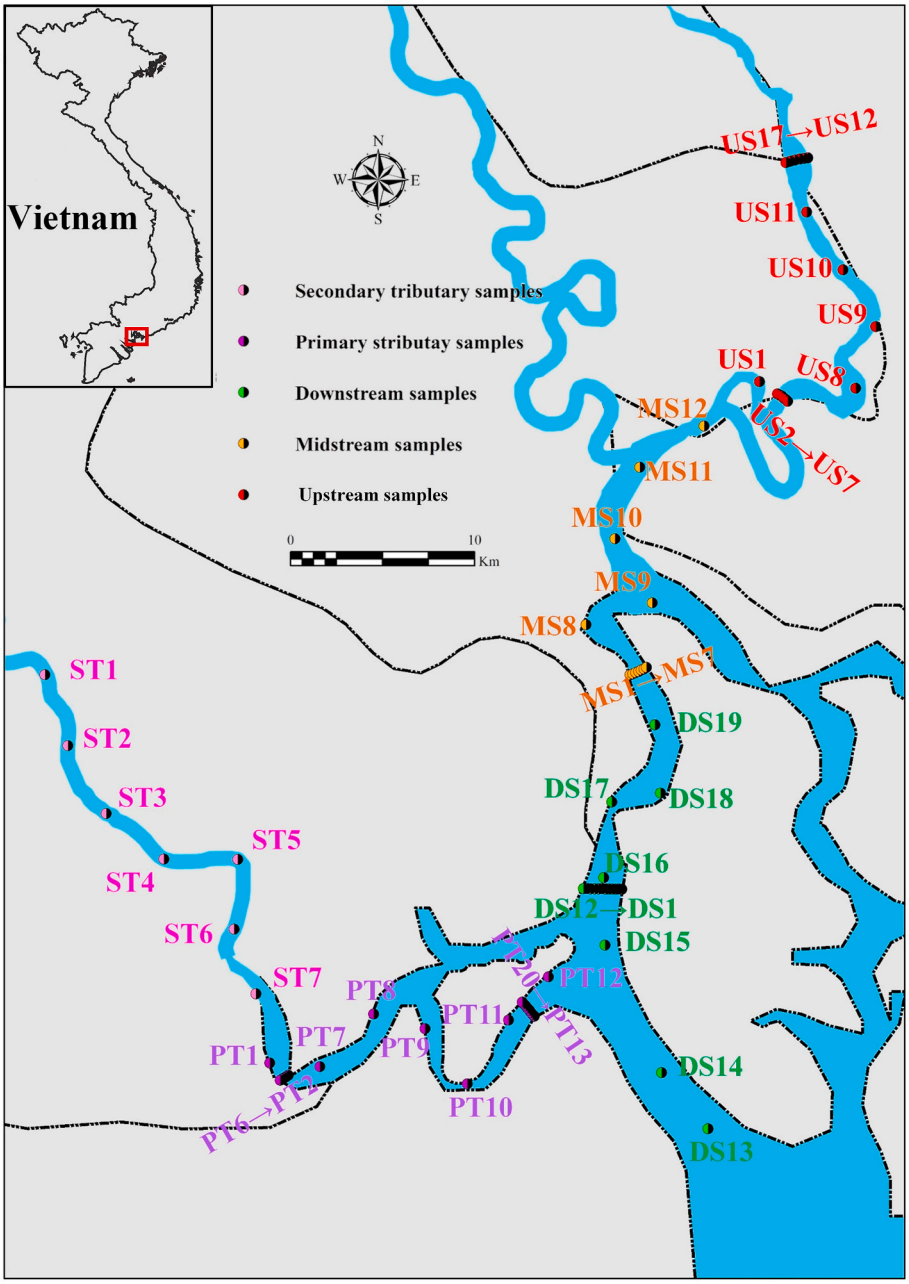

Fig. 1. Sediment sampling sites in the Dong Nai River System, Vietnam. US, upstream; MS, midstream; DS, downstream; PT, primary tributary; ST, secondary tributary.

and held for 0.5 min, and then ramped to 95% in 8.5 min and held for 3 min. The capillary voltage and desolvation temperature were set at 3000 V and 550 °C, respectively; the gas flows for desolvation, cone, nebulizer, and collision were 1000 L/h, 150 L/h, 7 Bar, and 0.13 mL/min, respectively. The compound-dependent parameters, including ion pairs, cone voltage, and collision energy, are provided in Table S1. Some analytes coeluted, and therefore their concentration sums (i.e., "PANA + PBNA" and "DBDPA + ODPA") were reported here.

The grain size and TOC content of sediments were measured using a laser scattering particle size distribution analyzer (Partica LA-960 A; Horiba Scientific, Kyoto, Japan) and a TOC analyzer (SSM-5000 A; Shimadzu, Kyoto, Japan), respectively.

2.4. Quality assurance and quality control (QA/QC)

A procedural blank was analyzed along with each batch of 8–10 samples to assess potential background contamination from our laboratory operation, while a matrix spike sample (prepared by adding 10 ng each of target compounds and surrogate standards to a random sediment sample from the corresponding two batches) was processed every two batches to evaluate the performance of our method. Measurable BDPA and IPPD were present in the procedural blanks at 0.28 ± 0.05 and 0.50 ± 0.19 ng (arithmetic mean ± standard deviation), respectively. To avoid overestimating chemical levels, data reported in this study were blank corrected by subtracting the corresponding average procedural blank on a mass basis. The method detection limits (MDLs) were defined as the average procedural blank level + 3 × standard deviation (n = 8), or the amount of chemicals producing a signal-to-noise ratio of 10 if the compound was not detected in the blanks (see Table S1). The repeatability of analytical method was evaluated by analyzing 15% of our samples twice; the relative standard deviations in concentrations of individual analytes between the duplicate measurements were all within

Table 1
Detection frequencies, medians, and ranges of concentrations of amino accelerators, amino antioxidants and their transformation products in sediments from the Dong Nai River System, Vietnam. MDL-method detection limit; DF- detection frequency.

Compound	DF (%)	Median (ng/g dw)	Range (ng/g dw)
Amino accelerators and antioxidants			
DPG	100	3.72	0.218–20.1
DTG	36	<MDL	<MDL-2.85
DPA	7.8	<MDL	<MDL-47.7
BDPA	18	<MDL	<MDL-1.59
DBDPA + ODPA	3.9	<MDL	<MDL-0.309
DODPA	32	<MDL	<MDL-0.998
diAMS	81	0.030	<MDL-0.082
PANA + PBNA	6.5	<MDL	<MDL-3.13
6 PPD	21	<MDL	<MDL-0.462
CPPD	34	<MDL	<MDL-0.230
DNPD	2.6	<MDL	<MDL-0.876
DPPD	0	<MDL	<MDL
IPPD	5.2	<MDL	<MDL-9.23
ΣAAL/Os	100	5.01	0.377–51.4
Amino antioxidants transformation products			
2-NO_2-DPA	58	0.301	<MDL-2.62
4-NO_2-DPA	31	<MDL	<MDL-1.67
4,4′–NO_2–DPA	0	<MDL	<MDL
DPB	64	1.66	<MDL-17.2
6 PPD-Q	38	<MDL	<MDL-0.170
∑AAOTPs	79	2.19	<MDL-18.6
Total			
ΣAll	100	7.69	0.378–51.7

25%. The recoveries of surrogate standards were 64 ± 6.5%, 93 ± 20%, 78 ± 7.9%, and 77 ± 7.4% for d_{10}-DPA, d_{10}-DPG, $^{13}C_6$-PBNA, and d_5-6 PPD-Q, respectively. The matrix spike recoveries of individual AAL/Os and AAOTPs ranged from 47% to 108%; to compensate for possible losses of target compounds during our sample treatment and for potential matrix effects, a surrogate standard was assigned to each analyte in terms of their similarity in the chromatographic retention time and chemical structure (see Table S1). The surrogate-adjusted matrix spike recoveries were in the range of 75–117%, more rational than the corresponding absolute recoveries. Therefore, the concentrations reported in this study were surrogate corrected. Another two AAOs, namely *N_1, N_4*-bis(5-methylhexan-2-yl) benzene-1,4-diamine and *N, N*-dibenzylhydroxylamine were also targeted but excluded from our analyte list due to the substantial residue in the blanks and the poor extraction recovery (<10%), respectively.

2.5. Statistical analysis

Plotting and statistical tests, including Kruskal-Wallis analysis of variance (ANOVA) with Dunn-Bonferroni post-hoc test for mean comparison and Kendall's tau test, were performed using OriginPro 2017 (OriginLab Corp.). Prior to statistical analyses, cells containing results below MDLs were substituted with MDL/sqrt (2), and all values were logarithmically transformed. The level of significance was set a $\alpha = 0.05$. The concentrations were reported on dry weight basis (ng/g dw) in this study.

3. Results and discussion

3.1. Profiles of amino accelerators and antioxidants in the DNRS sediments

AAL/Os were quantifiable in all the seventy-seven sediment samples, illustrating ubiquitous distribution of these compounds in the DNRS (see Table 1). The total AAL/Os concentrations (ΣAAL/Os) ranged from 0.377 to 51.4 ng/g. The most frequently detected congener was DPG (detection frequency: 100%), followed by diAMS (80.5%). It has been documented that DPG can be heavily released into the aquatic environment via multiple routes, particularly the storm runoffs over urban surfaces (Challis et al., 2021; Johannessen et al., 2022; Johannessen and HelmMetcalfe, 2021b; Peter et al., 2018). Similarly, diAMS was also prevalent in sediments from the Chicago Sanitary and Ship Canal and the creeks in Ontario, Canada, but at much higher concentration compared to our results (Lu et al., 2016; Wu and VenierHites, 2020). Although DPA was measurable in only six samples (three in the primary tributary, two in the downstream, and one in the midstream), its concentrations reached up to 47.7 ng/g, suggesting the enhanced discharge at certain points alongside the lower DNSR.

Data on occurrence of AAL/Os in sediments have remained scarce, particularly for sampling sites outside the United States and Canada (see Table 2). The AAO levels in sediments from the DNRS were generally 1–2 orders of magnitude lower than those from the North America, probably because of the modest production and use of these compounds in Vietnam, (Lu et al., 2016; Wu and VenierHites, 2020; Zhang et al., 2016; Zhang et al., 2020). However, considering the rapid urbanization and industrialization, the Vietnamese market demand for AAL/Os are projected to gain drastically in the near future. Despite that DPG was consistently detectable in our samples, its sediment-associated burdens have never been reported elsewhere, and thus future research is warranted to better unveil the fate of this commonly used AAL in the aquatic environment.

3.2. Transformation products of amino antioxidants detected in the DNRS sediments

The reducibility of AAOs makes them prone to be oxidized in the environment, and thus probing environmental fate of AAOTPs is also of high importance. DPA can be converted into 2-NO_2-DPA and 4-NO_2-DPA

Table 2
Comparisons of concentrations [median (range); ng/g dw] of amino antioxidants and their transformation products in sediments from the Dong Nai River System with those from elsewhere. Blank cells indicate that the analyte was not examined. MDL-method detection limit.

Reference	Continent	Country	Site	Year	DPG	DTG	DPA	BDPA	DBDPA
Wu and VenierHites (2020)	North America	United States	Chicago Sanitary and Ship Canal	2013			7.70 (<MDL-505)	2.03 (0.270–4.43)	10.3 (0.920–20.0)
Zhang et al. (2020)	North America	Canada	Ontario	2012			(0.94–1062)		
Lu et al. (2016)	North America	Canada	Southern Ontario	2012				(<0.0100–0.240)	(<0.200–4.70)
Zhang et al. (2016)	North America	Canada	Ontario	2012				1.27 (0.170–3.24)	0.280 (<MDL-6.48)
This study	Asia	Vietnam	Dong Nai River System	2018	3.72 (0.218–20.1)	<MDL (<MDL-2.85)	<MDL (<MDL-47.7)	<MDL (<MDL-1.59)	<MDL (<MDL-0.310)

by reacting with nitrogenous oxidants followed by recombinant on a benzene ring, and this process is likely to be enhanced under ambient atmospheric conditions, facilitated by the sunlight irradiation (Drzyzga, 2003; Liu et al., 2019; Wu and VenierHites, 2020). Meanwhile, DPB can be formed from the electrochemical dimerization of DPA, while it has also been synthesized to function as a building block of electronically conductive polymers and light-emitting diodes (Wu and VenierHites, 2020; Yang and Bard, 1991). It is worth noting that 6 PPD can undergo ozone oxidation and subsequently form 6 PPD-Q, which is of higher toxic than the parent compound (Tian et al., 2021, 2022).

Table 1 and Fig. 2b illustrate the concentrations and compositional patterns of AAOTPs in the DNRS sediments. The median ΣAAOTPs was 2.19 ng/g, even higher than the median of total AAO levels, i.e., 0.416 ng/g. DPB and 2-NO_2-DPA, with residues up to 17.2 and 2.62 ng/g, respectively, were the two predominant AAOTPs, collectively accounting for approximately 90% of the ΣAAOTPs in our samples. Comparable 2-NO_2-DPA levels were spotted in sediments from the Chicago Sanitary and Ship Canal, but these North American samples contained outstanding DPB levels with a median at 512 ng/g (Wu and VenierHites, 2020). Additionally, 6 PPD-Q was detected in 38% of our sediments, ranging from <MDL to 0.170 ng/g. There is little information on AAOTP residues in sediments, hindering us from a broader inter-regional comparison.

3.3. Spatial trends of AAL/O (TP)s in the DNRS sediments

The ΣAll were the highest in sediments from the DNRS downstream (median: 10.9 ng/g, range: 4.10–47.0 ng/g), followed by midstream (7.72 ng/g, 0.75–17.7 ng/g), primary tributary (7.41 ng/g, 1.17–51.7 ng/g), upstream (5.36 ng/g, 0.378–26.1 ng/g), and secondary tributary (2.73 ng/g, 0.66–9.63 ng/g) (see Fig. 2a and Table S3). Several congeners, like CPPD and DODPA, that barely detected in the upstream and secondary tributary sediments were more frequently detected in the downstream and midstream samples. According to the non-parametric ANOVA and post-hoc comparisions, the ∑All in the DNRS downstream sediments were significantly greater than those in the upstream and secondary tributary samples ($p < 0.05$, Figure S1). The inter-regional variations of ∑AAL/Os, ∑AAOTPs, and analytes with satisfactory detection frequencies (i.e., DPG, diAMS, DPB, and 2-NO_2-DPA), resembled that of ΣAll, exhibiting elevated concentrations in samples from the DNRS downstream, midstream, and/or primary tributary.

The highest ΣAll, largely constituted by DPA, were spotted at PT8 and DS18, both of which were close to port cities <35 km distant from the DNRS estuary and surrounded by a large area of croplands; apart from being an antioxidant, DPA has also been utilized as a pesticide (Robles-Molina et al., 2014), and therefore its outstanding concentrations at these two sites may result from the combination of domestic, industrial, and agricultural release nearby. The second highest ΣAll was found in sediments from MS8, adjacent to the downstream of Ho Chi Minh City, the most densely populated, urbanized, and industrialized area in Vietnam. These anthropogenic activities have incurred AAL/O(TP)s contamination in the DNRS. In contrast, sediments from the secondary tributary and upstream regions, absent from heavy anthropogenic activities, had relatively low ΣAll.

Significantly negative correlations were observed between the distance of a sampling site to the estuary and the ΣAll, ΣAAOTPs, and ΣAAL/Os, as well as several major congeners (see Fig. 3; the detailed Kendall's tau are given in Table S4), likely due to continuous discharge of these compounds alongside the DNRS. Meanwhile, distinctive hydrodynamics of the estuarine environment, particularly maximum turbidity zones generated by the accelerated resuspension and redeposition triggered by fluvial-tidal interactions, could also escalate sediment-associated AAL/O burdens in the DNRS estuary (Babut et al., 2019; Schwarzer et al., 2016; Wu et al., 2022). Additionally, our samples were collected during the wet season, and therefore the amplified rainfall-assisted transport of our analytes towards the estuarine area should not be overlooked (Tran and NguyenStrady, 2020).

The vertical patterns of ΣAll in six groups of transect samples are demonstrated in Fig. 2c, which were apparently influenced by anthropogenic activities, hydrodynamics, and mitigation by mangrove reserves. Regarding the upstream transect (US2-US7 and US12-US17), higher levels of AAL/O(TP)s were measured towards the western bank, likely attributed to its proximity to urban regions (Al An District and Ho Chi Minh City) potentially with more AAL/O(TP)s sources. Due to the dilution effect at central parts of stream, the gradient of ΣAll across transect sediments from the midstream (MS1-MS7) and downstream (DS1-DS12) generally exhibited a U-shaped curve with the reduced concentrations in the middle. PT13-PT20 presented a decreasing trend in ∑All towards the southern bank, beside the Can Gio Mangrove Biosphere Reserves in which human activities have remained limited. As for the other primary tributary transects, albeit that ∑All dropped southward from PT2 to PT5, an unexpectedly high level was detected at PT6 (mainly contributed by DPB; see Fig. 2c), which may suggest the presence of unknown source(s) and/or the preferential accumulation of our target compounds at this turning where multiple rivers converge.

3.4. Associations of AAL/O (TP) concentrations with dynamics of sediments

TOC content in the DNRS sediments ranged from 0.026 to 3.98%, with a median at 1.51% (see Table S2 for the detailed information). Significantly positive correlations were discovered between the TOC content and the sediment-associated concentrations of all frequently detected AAL/Os and AAOTPs (all $p < 0.05$; see Fig. 3 and Table S4), reflecting that the hydrophobic interaction between chemicals and the organic matter is a key force for the sorption of AAL/O(TP)s on

ODPA	DODPA	diAMS	PANA + PBNA	6 PPD	CPPD	DNPD	IPPD	2-NO_2-DPA	4-NO_2-DPA	DPB	6 PPD-Q
10.3 (0.920–20.0)	14.7 (2.43–28.8)	2.90 (<MDL-10.1)	1.00 (<MDL-1.64)	0.140 (<MDL-1.93)				0.460 (<MDL-0.460)	0.640 (<MDL-1.35)	512 (<MDL-1400)	
(0.360–9.60)	(0.0500–57.0)	(0.200–191)									
1.13 (<MDL-58.4)	9.78 (0.340–765.53)										
<MDL (<MDL-0.310)	<MDL (<MDL-0.100)	0.0289 (<MDL-0.0820)	<MDL (<MDL-3.13)	<MDL (<MDL-0.462)	<MDL (<MDL-0.230)	0.0126 (<MDL-0.876)	<MDL (<MDL-9.23)	0.300 (<MDL-2.62)	<MDL (<MDL-1.67)	2.54 (<MDL-17.2)	0.0174 (<MDL-0.170)

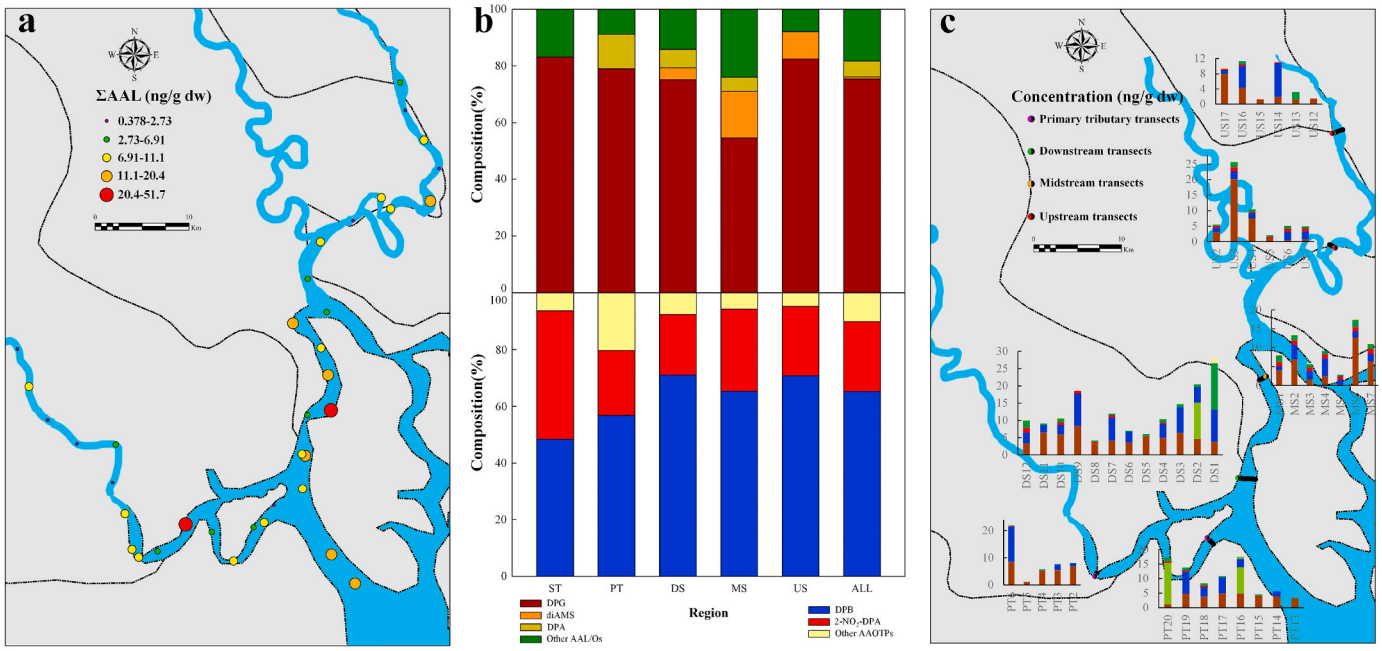

Fig. 2. Spatial distribution (a), compositional profiles (b), and gradients across transects (c) of amino accelerators, amino antioxidants and their transformation products in the Dong Nai River System sediments. DPG, 1,3-diphenylguanidine; diAMS, 4,4′-*bis*(1,1-dimethylbenzyl) diphenylamine; DPA, diphenylamine; DPB, *N, N*′-diphenylbenzidine; 2-NO_2-DPA, 2-nitrodiphenylamine.

sediments (see Table S1 for the octanol-water partition coefficient and water solubility of individual AAL/Os and AAOTPs) (Jin et al., 2023; Lu et al., 2016). Significantly higher TOC content was observed in the downstream sediments compared to the upstream samples, indicating a rise in active deposition due to the more intense fluvial-tidal turbulence towards the estuarine region. Therefore, the modest ∑All in upstream sediments may, to some extent, be ascribed to their low TOC content (Table S2). Considering the significant effect of TOC, we re-examined

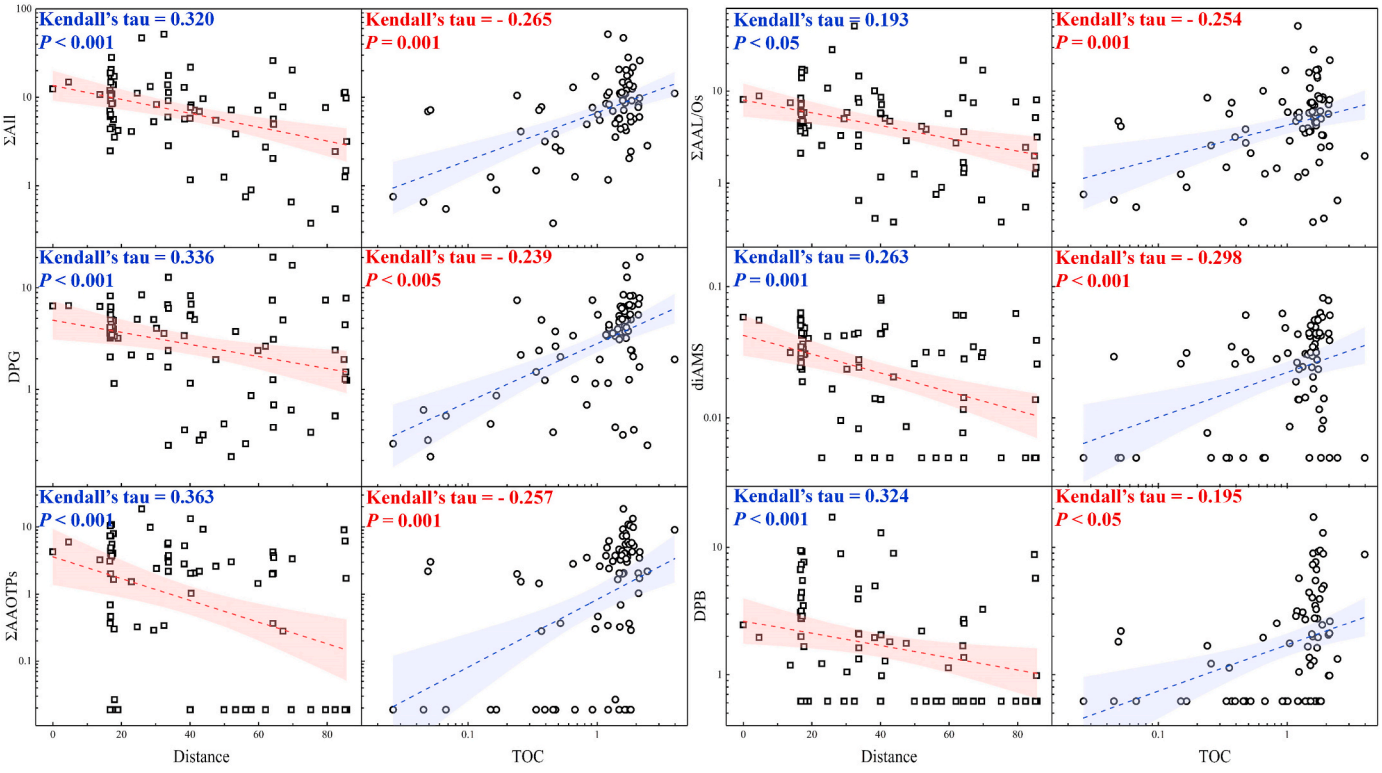

Fig. 3. Associations of concentrations (ng/g dw) of amino accelerators, amino antioxidants and their transformation products with the total organic carbon content (TOC; %) in sediments and with the distance (km) of a sampling site from the DNRS estuary. Dashed lines and shaded parts represent the linear regression of best fit and the 95% confidence intervals, respectively.

the regional patterns of TOC-normalized ∑All in DNRS sediments. The non-parametric ANOVA outcome revealed that the difference among different sections turned into marginally significant ($p = 0.098$, Figure S1), suggestive of the influence of TOC content on the sediment associated ∑All to certain extent.

The percentages of clay (particle diameter: <4 μm), silt (4–64 μm), and sand (>64 μm) ranged of 0.46–46.5% (median: 34.9%), 0.60–61.5% (46.9%), 0.20–98.9% (20.3%), respectively, in the DNRS sediments (see Table S2 for the detailed data). Affected by fluvial-tidal interactions, the particle size distribution varied among sampling sites, with the proportions of sand gradually declines seawards, suggesting the conversion of coarse particles into silt and/or clay. Concentrations of all prevalent AAL/Os and AAOTPs in our samples were significantly positively correlated with the fraction of clay and/or silt, except 2-NO_2-DPA (see Table S4). These results proved that the larger surface areas of finer particles can substantially upregulate the sorption capacity of sediments, rendering them more liable to accumulate organic contaminants (Badin et al., 2008).

4. Environmental implication

Previous studies have documented mortality, cytotoxic and neurotoxic effects of AAL/Os and AAOTPs [e.g., 6 PPD(-Q), DPA, and PANA] on aquatic organisms. Therefore, their pervasiveness in Vietnamese sediments is a cause for concern (Jin et al., 2023). However, the lack of reference values, like predicted no-effect concentration (PNEC), established for sediments have hindered us from quantitively and accurately evaluating the potential risks of these contaminants. Future research is urgently needed to comprehensively assess the toxicity of AAL/Os and their degradative derivatives to aquatic ecosystem.

The DNRS sediments have also been analyzed for other organic pollutants, allowing for the inter-compound comparisons. The levels of AAL/Os we observed were generally two orders of magnitude lower than those of OPEs from the same sampling sites (Ma et al., 2022). On the contrary, our AAL/Os exhibited greater concentrations in the DNRS sediments than two notorious PFAS, namely perfluorooctanoic acid and perfluorooctane sulfonic acid (Lam et al., 2017), and rivalled dichlorodiphenyl trichloroethane (DDT) (Nguyen et al., 2019), suggesting that AAL/Os may have become one of the epidemic environmental contaminants beneath Vietnamese aquatic systems. Therefore, the toxic effects from co-existence of multiple AAL/Os and/or other contaminants should be taken into account for further investigation.

5. Conclusions

This is the first comprehensive report on the occurrence and spatial patterns of AAL/Os and their transformation products in sediments collected beyond the North America. Compared to previous studies conducted elsewhere, ΣAll in the DNRS sediments were modest, with DPG, diAMS, DPB, and 2-NO_2-DPA being the predominant congeners. The peak ΣAll were spotted around urbanized and agricultural regions, suggesting the appreciable human impacts. Moreover, the vertical distribution of our transect samples also highlighted that, apart from anthropogenic activities, fluvial-tidal interactions and mitigation by pristine mangrove reserves may also cause bank-specific accumulation of these compounds. Additionally, our data also confirmed the associations of AAL/O(TP)s concentrations with the characteristics of sediments. The present study provides useful information on distribution of this suite of emerging contaminants beneath the aquatic environment worldwide.

Credit author statement

Ruihe Jin: Data curation, Formal analysis, Visualization, Writing-original draft; Yue Li: Investigation, Data curation, Writing-review & editing; Yoshiki Saito, Zhanghua Wang, Thi Kim Oanh, Van Lap Nguyen: Sample collection, Writing-review & editing; Jing Yang: Writing-review & editing; Min Liu: Funding acquisition, Writing-review & editing; Yan Wu: Conceptualization, Funding acquisition, Investigation, Supervision, Validation, Writing-review & editing.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envres.2023.115712.

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