Microplastic as a Vector for Chemicals in the Aquatic Environment. Critical Review and Model-Supported Re-interpretation of Empirical Studies.

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Abstract

The hypothesis that 'microplastic will transfer hazardous hydrophobic organic chemicals (HOC) to marine animals' has been central to the perceived hazard and risk of plastic in the marine environment. The hypothesis is often cited and has gained momentum, turning it into paradigm status. We provide a critical evaluation of the scientific literature regarding this hypothesis. Using new calculations based on published studies, we explain the sometimes contrasting views and unify them in one interpretive framework. One explanation for the contrasting views among studies is that they test different hypotheses. When reframed in the context of the above hypothesis, the available data become consistent. We show that HOC microplastic-water partitioning can be assumed to be at equilibrium for most microplastic residing in the oceans. We calculate the fraction of total HOC sorbed by plastics to be small compared to that sorbed by other media in the ocean. We further demonstrate consistency among (a) measured HOC transfer from microplastic to organisms in the laboratory, (b) measured HOC desorption rates for polymers in artificial gut fluids (c) simulations by plastic-inclusive bioaccumulation models and (d) HOC desorption rates for polymers inferred from first principles. We conclude that overall the flux of HOCs bioaccumulated from natural prey overwhelms the flux from ingested microplastic for most habitats, which implies that microplastic ingestion is not likely to increase the exposure to and thus risks of HOCs in the marine environment.

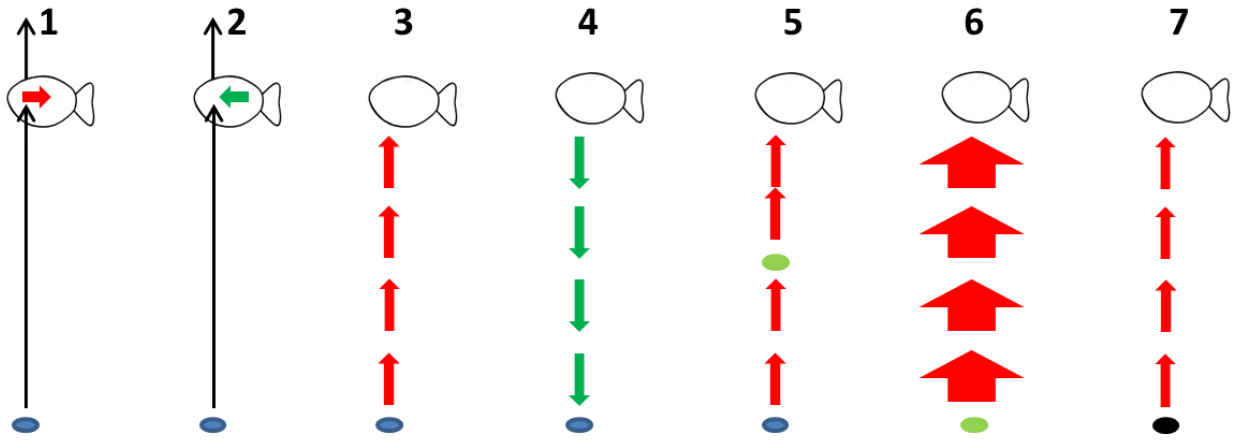Key words – bioaccumulation, microplastic, marine animals, marine debris, hydrophobic organic chemicals

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Introduction

The contamination of the environment with plastic is considered highly undesirable for ethical and esthetical reasons and is generally considered to be a major threat for the health of aquatic ecosystems.[1] It has been demonstrated that numerous species ingest plastic debris or become entangled by it.[2,3,4,5] The physical damage to wildlife caused by larger forms of plastic (> 5 mm in size) is also well documented, although clear indications of harm at the level of populations or communities have not been convincingly demonstrated. Still, the impact of micro-plastics (< 5 mm) remains under investigation.[6,7,8]

Because the research examining microplastics is still in its infancy, studies measuring their fate and effects use widely different methods and approaches. As such, they provide fragmentary information and often use high microplastic concentrations and/or other non-environmentally relevant conditions to test for effects. Although this has resulted in several recent publications demonstrating new evidence of adverse effects, the body of evidence emphasises the need to harmonise methodologies and design tests using environmentally relevant conditions.[7] Addressing environmentally relevant conditions is a key prerequisite for a scientifically sound assessment of the hazard and risks of microplastics in the environment, which is key to really understand the possible risks of microplastics at the level of populations or communities.

One potential hazard stems from the fact that plastic particles contain or efficiently absorb hydrophobic organic chemicals (HOCs), which includes non-covalently bound additive ingredients.[9,10,11] This has sparked hypotheses (1) on how microplastic contributes to the transport of HOCs, and (2) whether the ingestion of microplastic contributes to the bioaccumulation of HOCs by marine animals.[12,13,14,15,16,17,18] Both ideas have led to considerable attention and debate. The ability of polymers to act as a source of HOCs to

80   organisms has been recognized for a long time as it is the essence of the passive dosing

81   approaches used in ecotoxicology.[19,20] The past years this has been reconfirmed in the context

82   of marine plastic debris by a series of laboratory studies that used microplastic as the sole

83   source of HOCs.[21,22,23] The studies in general support the above hypotheses, i.e. that

84   microplastics are a vector and source of HOCs to marine organisms.

85   However, the debate has formed from questions regarding whether plastic is a substantial

86   source of these toxic chemicals to aquatic organisms relative to other sources in the

87   environment. After all, given the low abundance of plastic particles relative to other media

88   present in the oceans, exposure to these HOCs via plastic is probably of less importance than

89   via natural pathways.[7,24,25,26,27,28] Some recent papers argue that plastic is (potentially) an

90   important exposure route because the affinity of HOCs for plastic is high.[12,21] This is likely

91   overruled when considering that the importance of plastic as a carrier is also dependent on the

92   abundance of plastic compared to that of other carrier media such as water, suspended organic

93   particulates or natural diet and prey items many of which have partition coefficients that are

94   similar to that of plastic.[29] Laboratory dietary exposures that demonstrate that plastic debris

95   can be a vector of HOCs to marine organisms have not truly tested hypotheses regarding the

96   relative importance of microplastics in comparison to other sources occurring in real

97   environments. Several recent quantitative assessments, modelling studies and reports have

98   concluded that the contribution of plastic to chemical fate and transport of HOCs in the

99   oceans, and to bioaccumulation of these chemicals by marine organisms is probably

100   small.[24,25,26,28,30] This perceived dichotomy in the discussions of various published studies is

101   confusing and hampers progress towards scientific consensus regarding the actual risks of

102   microplastics. In turn, this may hamper policy development and the prioritization of research

103   needs and remediation measures.

The aim of this paper is to critically review and synthesize the literature concerning the role of plastic as a carrier/vector of chemicals. This includes reviewing empirical and modelling studies, as well as incorporating the lessons learned from the behaviour of sorbents other than plastic (e.g. organic matter, black carbon, activated carbon, carbon nanomaterials, and passive dosing or - sampling polymer materials) that share the same principles with respect to the binding of HOCs. We also apply models to reinterpret laboratory studies in an attempt to unify various study results into a unified interpretation framework.

To reach our objective, we first discuss the state of (non-)equilibrium of the binding of HOCs to microplastics in the marine environment. Plastic particles can only constitute an ongoing source of HOCs to the water or to aquatic organisms if the HOC concentration in these particles is sufficiently high (i.e. higher than equilibrium) compared to that in the water or in the organisms. This calls for a comparison of HOC (de-)sorption half-lives and of the residence times and age of plastic particles in the oceans. As far as we know, no such assessment has been performed yet. Second, we discuss the average distribution of HOCs across media in the ocean, a distribution that can be assessed by accounting for (1) the relative abundances of these media, and (2) the relative affinities of HOCs for these media. Assessment of this distribution under environmentally realistic conditions is crucial in order to understand the relative importance of plastic (compared to other media) in the transport of HOCs or in the bioaccumulation of HOCs by marine organisms. A few earlier studies have provided a similar distribution analysis,[24,30] however, without taking into account all known media, such as dissolved organic carbon, colloidal carbon, black carbon, detritus and plankton. Third, we discuss recent studies that document transfer of HOCs from plastic to marine organisms or vice versa, and provide novel model calibrations using data from these studies. This provides a mechanistic interpretation of the results of these previous empirical studies, unifies empirical and model-based approaches regarding the same research questions,

129 and allows for extrapolations to natural conditions in case these empirical studies were not

130 fully mimicking natural conditions. Furthermore, past literature is evaluated for

131 environmental relevance, i.e. extent of using realistic concentration ranges and completeness

132 with respect to covering processes that are known to occur in the field. Finally, we discuss the

133 implications of our analysis for risk assessment and suggest priorities for future research.

The state of equilibrium of HOC partitioning in the oceans

135 **Equilibrium sorption of HOCs to plastics.** HOCs are subject to partitioning across

136 environmental media such as water, sediment, biota, air, and since the 1950's: plastic.[31] The

137 equilibrium partitioning coefficient for sorption to plastics K_{PL} [L/kg], is defined as:[12,32]

138 $$K_{PL} = C_{PL}/C_W \hspace{4cm} (1)$$

139 where C_{PL} [µg/kg] and C_W [µg/L] are the concentrations in plastic and water, respectively. Eq

140 1 is important to address the question whether HOCs are sorbed to microplastic or are

141 released by microplastic, because the spontaneous transfer of HOCs always occurs in such a

142 direction that the actual concentration ratio (C_{PL}/C_W) approaches the value of K_{PL}.[15] For

143 instance, if $C_{PL}/C_W > K_{PL}$, then desorption from the plastic to water takes place and vice versa.

144 The time needed to reach equilibrium depends on the molecular properties of the HOC, the

145 properties of the seawater and the microplastic, as well as on the volumes of these

146 compartments. The kinetics of sorption to microplastic is beyond the scope of this review, but

147 it is obvious that sorption equilibrium may exist for microplastics that reside in the ocean for

148 already a long time, whereas equilibrium may not exist for microplastics that were released

149 recently. This means that two aspects need to be compared (1) the age distribution of

150 microplastics currently present in the oceans, and (2) the sorption equilibration times of

151 representative HOCs.

Estimating the age distribution of microplastics in the oceans. Annual world production

data for plastics are well known and show a gradual increase from 1.7 million tonnes in 1950

to about 299 million tonnes per year in 2013 (Figure S1, data from[31]). The curve can be

smoothed using a 2nd order polynomial (Figure S1), which accurately captures the trend but

averages some small fluctuations caused by stagnations in the world economy in the 1970's,

1980's and recently in 2007. It is commonly assumed that a more or less constant fraction of

the world plastic production ends up in the oceans.[33] The few million tonnes of plastic emitted

in the first years of production have an 'environmental age' of about 60 years, whereas the

production of 299 million tonnes in 2014 has by definition an age of less than a year. By

combining the annually emitted volumes per year with the age of these yearly volumes (i.e.

present year minus year of emission) an age distribution for the cumulative quantity of

emitted plastic can be calculated (Figure 1). Because a more or less constant fraction of the

yearly world production ends up in the oceans, Figure 1 also represents the expected age

distribution for ==all plastic== in the oceans. The calculation (for 2015) shows that about 50% of

the plastic has been present in the oceans for more than 13 years, whereas 80% and 90% of all

the plastic is older than 4 and 2 year, respectively (Figure 1). If we use European production

data[31] the age distribution is similar, however, it shows that 50% and 90% of the produced

plastics has been present in the European seas for more than 17 years and 3 years, respectively

(Figure 1). In reality, the oceans do not represent one uniform compartment.[34] However,

mixing within areas or in gyres can be considered more homogeneous. Furthermore, sources

and types of plastics do not substantially differ across the globe. Microplastics are considered

ubiquitous global contaminants, whereas transport and mixing causes the spreading of

microplastics in the oceans, with contamination of even very remote areas as a

result.[34,35,36,37,38] Coastal areas may contain relatively 'young' plastic particles, yet these areas

also receive aged plastics from remote areas. Indeed beached plastic has been shown to also

177   come from remote sources. Remote areas like the Arctic[35] or deep sea sediments[39] are further

178   away from anthropogenic sources, implying that they may have a higher share of older

179   microplastics. We conclude that the age distribution of microplastic in a given area probably

180   does not show a strong spatial heterogeneity and that the age distribution as given in Figure 1

181   is roughly uniform across the different major oceanic regions.

182   **Comparing HOC equilibration times for microplastic with the age of plastic in the**

183   **oceans**. Several studies have addressed the sorption kinetics under realistic field conditions

184   and by using field-relevant types of microplastics. These studies generally reported desorption

185   half-lives of weeks to 1-2 year for many types of 0.5 – 5 mm sized microplastic for the most

186   hydrophobic classes of HOCs, like PCBs and PAHs[40,41,42], with shorter half-lives for the

187   smaller microplastics. Sorption of more hydrophilic compounds generally will be faster,

188   which means that the vast majority of HOCs will be at equilibrium after 2 years, whereas for

189   some very hydrophobic HOCs it may take longer to fully reach equilibrium, especially for the

190   larger macroplastic particles (i.e. > 5 mm). These sorption equilibration times can now be

191   compared to the ages of plastic in the oceans. It follows from the age distribution (Figure 1)

192   that 80 to 90 % of the plastic is older than 2 to 4 years and therefore will be at or close to

193   sorption equilibrium for all HOCs to be considered, including additives and plasticizers.

194   Virtually all plastic will be at equilibrium for the majority of the HOCs with half-lives in the

195   order of months. The remaining cases, i.e. the very hydrophobic HOCs sorbing to the fraction

196   of larger 'young microplastic' particles, are in an intermediate state with 50% of equilibrium

197   reached as the best estimated intermediate value. The above estimation most probably under-

198   predicts the magnitude of equilibrium for aged and free-floating microplastics. After all, the

199   above sorption half-lives have been assessed for microplastics in a rather pristine state, based

200   on exposures of up to a year at most. It is known that over longer time scales, embrittlement

201   and abrasion lead to the formation of much smaller particles, cracks and pores[37] which

202 increases the kinetics rates of sorption due to larger surface area and shorter intrapolymer

203 diffusion paths.[32,42] The slow fragmentation of plastic implies that generally the older plastic

204 also will be the smaller and thus more equilibrated microplastic, which (because of its smaller

205 size) also is likely to be bioavailable for a wider range of aquatic organisms. Furthermore, part

206 of the aforementioned sorption half-lives were measured for microplastics enclosed in bags

207 with 1.3 and 10 mm mesh,[41] which probably reduced hydrodynamic flow around the particles.

208 This means that the sorption kinetics might have been faster when the plastic particles would

209 have been floating freely. A recent paper measured concentrations of PAHs in both the plastic

210 and water phase in the North Pacific gyre and found that partitioning of PAHs between plastic

211 and water was virtually at equilibrium.[43] In summary, we conclude that with respect to

212 sorption of HOCs, sorption equilibrium is a valid general assumption for the majority of

213 microplastics currently present in the oceans.

214 The multi-media distribution of chemicals in the oceans

215 **The need for calculating the distribution of HOCs across environmental media**. Many

216 papers argue that plastic is highly abundant in the oceans and has very strong binding

217 properties for HOCs, such that plastic probably plays an important role in the transport and

218 transfer of HOCs in the oceans, and in the bioaccumulation of HOCs by marine

219 biota.[12,13,17,21,22,23] This reasoning links the potential risk and harm of plastic to its presumed

220 role as a carrier of chemicals. This role, however, is also played by all other environmental

221 media such as water, air[30,32], and - for HOCs – other carbon-based media such as dissolved

222 organic carbon, organic colloids, black carbon and biota.[24,32,44,45,46] Therefore, it is important

223 to know the relative quantity of chemicals sorbed by plastics in the oceans, compared to the

224 quantity held by these other media. Marine organisms ingest plastic together with regular prey

225 items, including the abundant detritus fraction, and phyto- and zooplankton species. Exposure

226 to HOCs by the ingestion of plastic may be substantial if the mass of HOC in the plastic is

227 sufficiently large compared to these other 'diet' components. This constitutes another reason

228 to assess the relative quantity of HOCs in plastics compared to other solid phases. This

229 relative quantity is governed by re-partitioning phenomena among environmental media,

230 including plastic. These media thus act as communicating vessels for chemical transfer.

231 **Plastics and other environmental media as communicating vessels**. The principles of

232 partitioning of HOCs across environmental media have been assessed extensively in

233 literature[32,47,48], including re-partitioning upon addition or removal of an environmental

234 sorbent or anthropogenic sorbents[49,50] For instance, addition of sediment in a laboratory

235 bioaccumulation test system reduced chlorobenzene uptake by fish. This reduction could be

236 fully explained by the quantity of sediment added and the chlorobenzene K_P for the

237 sediment.[51] Three decades ago, the effect of activated carbon addition on PCB

238 bioaccumulation by goldfish was tested in the laboratory, resulting in a 70.9−99.9% reduction

239 in PCB fish concentrations.[52] Adding activated carbon as a remediation method for sediments

240 was also tested in the field, showing a 20-fold reduction in PCB bioaccumulation in golden

241 orfe.[53] Similarly, plastics have been studied as cleaning materials for the remediation of soils

242 and sediments.[54] Such applications require a sufficient quantity of sorbent material in order to

243 cause significant repartitioning and immobilization of HOCs. However, in other applications

244 plastics also have been applied in quantities that are deliberately low compared to those of

245 other environmental media. Polymers like LDPE, POM or silicone rubbers have been applied

246 as negligible depletion passive samplers[9,55,56], where the ability of plastic to reach an HOC

247 equilibrium state in weeks or months (see previous section) is used to infer freely dissolved

248 HOC concentrations in water.

249 These are just a few examples of a vast body of literature showing the reversibility of HOC

250 partitioning among media including polymers, where the direction of transfer is determined

251 by a concentration ratio being higher or lower than the equilibrium partition coefficient. Some

252 recent studies have reconfirmed these phenomena in the context of marine debris. For

253 instance, the addition of (clean) plastic to laboratory systems with a finite quantity of HOC

254 was observed to cause a decrease in the HOC concentration in the marine organisms being

255 tested.[12,13,22] These authors, however, acknowledged that the abundance of plastic in the

256 marine environment would be too low to cause a similar cleaning effect *in situ*, which also is

257 likely for the opposite process. Below we discuss studies that have addressed this question

258 and provide an update of such calculations based on most recent data.

259 **The distribution of HOC across environmental media in the ocean**. The relative role of an

260 environmental compartment in the oceans in transport or transfer can be assessed by

261 calculating the quantity of HOC held by that compartment relative to the other

262 compartments.[24,30,32] The mass of HOC in a medium is likely to be high if that medium is

263 abundant. Likewise, the mass of HOC in a medium is high if the affinity of the HOC as

264 quantified by the partition coefficient K_P is high for that medium. The total mass of a HOC in

265 a volume within a gyre, sea or ocean (Q_T) can be expressed as

266 $$Q_T = C_W V_W + C_W \sum_{i=1}^{n} M_i K_{P,i} + C_W M_{PL} K_{PL} \qquad (2)$$

267 The first term represents the HOC mass in the water with V_W and C_W being the volume of

268 water and the HOC concentration in water, respectively. The second term accounts for the

269 masses in 'n' non-aqueous compartments like dissolved organic carbon, organic colloids,

270 black carbon, detritus, phytoplankton and zooplankton (in this case n=6). Biota at higher

271 trophic levels could be included but, even though they may have higher levels of HOCs due to

272 biomagnification, are not accounted for here because of their negligible mass compared to

273 that of the other solid phases present.[57] In this term, M_i represents the mass of the

274 compartment in the ocean and $K_{P,i}$ the partition coefficient for sorption of the HOC to solid

275   phase 'i', based on the assumption of sorption equilibrium as motivated in the previous

276   section. Similarly, the last terms account for the mass of HOC present in plastic, with M_{PL} the

277   mass of plastic in the ocean compartment. In essence, the products $M \times K_P$ determine the

278   relevance of a phase. For instance, although the affinity of a HOC for plastic could be very

279   high, the role of plastic in transfer and accumulation would still be negligible overall, if the

280   abundance of plastic is low relative to the abundance of other media present. The fraction of

281   the mass of HOC in plastic can be expressed as a fraction of the total mass of HOC as (C_W

282   cancels out):

283   $$M_{PL}K_{PL}/(V_W + \sum_{i=1}^{n} M_i K_{P,i} + M_{PL}K_{PL}) \hspace{3cm} (3)$$

284   Using this type of calculations, Zarfl and Matthies[30] calculated mass fluxes of PCBs, PBDEs

285   and perfluorooctanoic acid (PFOA) to the Arctic. Fluxes for transport of water, plastic and air,

286   were combined with concentrations of HOCs in these media (either estimated from

287   partitioning data, or measured), in order to obtain fluxes of the HOCs. They calculated that

288   the fluxes mediated by plastic were 4 to 6 orders of magnitude lower than those mediated by

289   oceanic currents and air. Similarly, Gouin et al[24] defined a representative coastal marine

290   ecosystem in which plastic was present. Using the abundances of media and a wide range of

291   HOC partitioning coefficients, they showed that sorption to polyethylene (PE) would occur

292   for a negligible <0.1 % of the mass of the chemicals. This means that the plastic abundance

293   currently present in coastal waters is insufficient to cause a meaningful redistribution of

294   HOCs from the oceanic environment to the plastic.

295   Recently, new data on the abundance of plastics suggest that there is currently 268,940 tonnes

296   of plastic floating in (all) oceans, of which 35,540 tonnes are < 4.75 mm microplastics.[58]

297   Using these data we calculated the overall average distribution of HOCs across media in the

298   oceans. This update also included media that were thus far not accounted for, like organic

299   colloids, black carbon and zooplankton, next to the common phases water, dissolved organic

300   carbon (DOC) and phytoplankton. Several studies have highlighted the sources and

301   abundance of black carbon in the oceans.[59,60,61,62] For the present calculations, abundances of

302   black carbon were estimated using data provided by Pohl *et al.*[62], and for the other organic

303   carbon phases data were taken from Couwet (1978)[63] (Figure 2A). The abundances of these

304   phases range from 2.7×10^8 kg for plastic[58] to 1.4×10^{21} kg (or ~L) for water[64] (Figure 2A).

305   This implies that an estimate of the average 'whole ocean' concentration of plastic would

306   equate to ~2 ng/L. We used one of the highest values for K_{PL} measured for a HOC on

307   microplastic; 10^7 L/kg.[10] Several studies have shown that the suspended sediment partition

308   coefficients $K_{P,i}$ on an organic carbon basis are similar[10] or higher[29] than those reported for

309   microplastic. Nevertheless, following Zarfl and Matthies,[30] the organic carbon partition

310   coefficients $K_{P,i}$ were set at a conservative value of $0.01 \times K_{PL}$, whereas for black carbon they

311   were set at a conservative $100 \times K_{PL}$.[45,55,65] This implies that although the masses of plastic and

312   black carbon are estimated to be about equal, the mass of HOC sorbed to black carbon would

313   be about two orders of magnitude higher than to plastic in the ocean (Figure 2B). The

314   distribution calculated using these data and Eq 3 shows that most HOCs are present in the

315   water (Figure 2B, Table SI-1), which implies that oceanic water currents constitute the main

316   transport medium for HOCs across the ocean. Plastic binds 1.93×10^{-4} % of this model HOC

317   (Table SI-1), a percentage that will even be smaller for other combinations of HOC and

318   plastic because we used a worst-case calculation (i.e., highest possible K_P for plastic, low

319   estimates for K_P for the other carbon phases). So, although plastic concentrates HOCs by

320   factors up to 10^7 from the water, plastic is still irrelevant as a carrier phase because the mass

321   of water is about a factor of 10^{13} larger than that of plastic. Even if plastic concentrations

322   (locally) would be orders of magnitude higher than the 'whole ocean' average used in our

323   calculation, this would not change the large excess of other media compared to plastic.

324 Solid particles, however, may be more important for the vertical transport of HOCs because

325 of their tendency to settle. However, a similar calculation excluding the non-settling water and

326 DOC shows that colloids, detritus and black carbon nanoparticles would still dominate the

327 solid phase speciation, with only 2×10^{-2} % of HOC bound to plastic (Table SI-1). In

328 summary, these simple calculations confirm the results of earlier studies,[24,30] showing that the

329 fraction of HOC held by plastic is negligible compared to that held by other media, which

330 implies that plastic-mediated transport is generally unimportant in terms of HOC masses. As

331 discussed in the previous section, most plastic particles containing additives at higher than

332 equilibrium concentrations will reach an equilibrium, given their long transport and residence

333 times in the oceans, rendering these calculations also applicable to these chemicals.

334 **The role of microplastic in bioaccumulation of HOCs to marine aquatic**

335 **organisms**

336 **Processes determining the relative importance of microplastic as a carrier of HOCs**

337 **under environmentally relevant conditions.** The mechanisms that explain the effect of

338 microplastic on bioaccumulation in marine organisms have been summarized in several recent

339 reviews, [13,14,15,16,24,25,26,28,46] whereas numerous papers address these processes separately or in

340 detail. Here we give a brief summary of these isolated mechanisms that affect the role of

341 microplastic as a carrier of HOCs (Figure 3), and provide selected references supporting the

342 occurrence of these mechanisms:

343   1. Plastic being ingested leading to HOC transfer from the plastic to the organism

344   ('absorption').[21,22,23,25,66]

345   2. Plastic being ingested leading to increased excretion of HOC from the organism

346   ('cleaning').[24,25,28,67]

347   3. Plastic acting as a source of HOCs in the environment, which subsequently are

348   available for dermal uptake or uptake by the gills ('source').[13,19,20,24,25]

349   4. Plastic accumulating HOCs from the seawater and organisms ('sink').[12,22,24,25,54]

350   5. Desorption of HOCs from plastic followed by uptake by natural organic particles or

351   prey, followed by ingestion of prey ('indirect source - dietary'). [44,46,68]

352   6. Uptake of HOC by ingestion of regular (i.e. non-plastic) prey items ('dietary').[44,46,68]

353   7. Uptake of HOC by dermal transfer or transfer across gills from other sources than the

354   plastic ('other source dermal').[44,46,68]

355   Mechanism 1- 4 are common for all non-digestible sorbents and determine the net uptake flux

356   from the plastic. Studies that consider the mechanisms 1-4 can provide 'proof of principle' or

357   can provide mechanistically relevant knowledge regarding the uptake of HOCs from plastic.

358   Processes 1-4 are supported by several empirical and modelling studies as indicated.

359   Mechanism 2 is less well-recognized in the literature on plastic debris and may need further

360   experimental validation. However, the process is generally well known for animals and

361   humans as it is the essence of medical treatment after acute poisoning with HOCs.[69] Just like

362   plastic,[67] liquid paraffin,[70] olestra[69,71] or activated carbon[72] are non-digestible, non-absorbable

363   lipophilic polymeric phases, which have been shown to increase the excretion and decrease

364   the body burden of HOCs.[24] Processes 5 and 6 relate to natural pathways of HOC uptake by

365   organisms yet they are crucial to assess the relative importance of processes 1- 4 under

366   environmentally realistic conditions. Process 7 recognizes that HOCs originating from other

367   sources than plastic may be taken up from the water. A recent study for instance, showed that

368   plastic is an important yet not the only source of bisphenol A (BPA) from waste-handling

369   facilities, and that BPA in the leachate from the facilities was freely dissolved and not bound

370   to microplastics.[73] All of these studies have helped to further understand the isolated

371   processes. However, to answer the questions whether plastic is a relevant carrier of HOCs in

372 the natural environments, we have to evaluate *all* processes 1 – 7 occurring in realistic

373 environments. This also implies that studies that do not explicitly consider the processes

374 under 5-7, or that neglect the cleaning mechanisms related to plastic (2 and 4) are inherently

375 less informative for answering that question.

376 **Overview and critical evaluation of research approaches.** Studies that assessed the role of

377 plastic as a mechanism for bioaccumulation in the field have been reviewed recently.[15,16] We

378 are aware of 13 studies (excluding seabirds) that somehow addressed the role of plastic in the

379 bioaccumulation of HOCs in the context of pollution with marine debris (Table SI-2). All

380 these studies provide relevant information concerning this question; however, they differ in

381 their research approach and in the extent to which they reflect environmental realism. An

382 overview of these studies that characterises the extent to which various processes and natural

383 conditions are accounted for, is provided as Supporting Information (Table SI-2). We divide

384 these studies in three main categories each having their specific merits and flaws, and discuss

385 these hereunder.

386 *Laboratory studies*. A first category of empirical studies has provided evidence for the

387 transfer of HOCs from plastic to biota under controlled laboratory conditions[21,22,23,66,67,74] and

388 has been reviewed before.[12,14,16] One study[74] was performed under environmentally relevant

389 conditions with all exposure pathways accounted for, and reported an increase in

390 accumulation of Σ PCBs in lugworms of 29%. This percentage, however, decreased at a

391 higher plastic dose and it was concluded that the effect could not be attributed to ingestion of

392 plastic.[25,74] In several other studies, clean[21,22,23] or relatively clean organisms[66] were exposed

393 to rather high quantities of HOC spiked plastics, which forces transfer of the HOCs to the

394 organism. Such experiments can be viewed as chemical bioaccumulation or toxicity tests

395 where plastic acts as vector for administering the contaminants to the test chemicals, invoking

396 effects of these chemicals once toxicity thresholds are exceeded. These non-equilibrium test

397   designs confirm earlier work showing that polymers will act as a source or carrier material for

398   HOCs towards media with lower than equilibrium fugacity. For instance, passive dosing is a

399   technique increasingly being used in ecotoxicology to control aqueous phase exposure

400   concentrations during toxicity tests.[19,20] The main merit of these non-equilibrium set-ups is

401   that HOC transfer from plastic to biota is studied at a maximum possible HOC gradient

402   between plastic and organism, with a limited or negligible role of other uptake pathways like

403   uptake from water or food. This potentially allows the quantification of the parameters that

404   drive chemical transfer from the plastics in the gut, parameters that are urgently needed.[24,25,28]

405   Because the aforementioned laboratory studies observed bioaccumulation or even adverse

406   effects of chemical exposure, they concluded that ingestion of plastic potentially constitutes a

407   hazard in the oceans. This reasoning, however, is not without problems. First, use of freshly

408   spiked or field-contaminated plastics in clean water leads to chemical desorption to the water,

409   leading to dermal uptake. Therefore, to confirm that the bioaccumulation was from *ingestion*,

410   zero aqueous phase concentrations need to be demonstrated, these data are, however, not

411   provided in these studies (e.g,[21,22,23,66,74]). Second, the argument that ingested plastics will act

412   as a carrier is correct for chemicals that reside in the plastic at higher than equilibrium

413   fugacity (like additives), which however was shown to occur for only a minor fraction of the

414   plastics in the marine environment, based on desorption half-lives (see above). Third, for

415   chemicals that occur in plastic at lower than equilibrium fugacities, plastic would have an

416   opposite, i.e. beneficial effect. This effect would decrease the hazard due to plastic and

417   usually is not addressed in these studies. Fourth, some studies did not consider uptake from

418   natural exposure routes.[21,22,23] In most environmentally realistic settings, the concentrations of

419   plastic would be far lower than those used in most of these studies. These studies therefore

420   underestimate the role of natural routes. For instance, the first mentioned experiment[74] was

421   performed under realistic conditions yet the authors could not clearly show that plastic acted

422 as a carrier for HOCs. Fifth, to confirm the hypothesis that plastic acts as a carrier of toxic

423 chemicals upon ingestion, ingestion of the plastic should be experimentally confirmed, which

424 however was not the case for some studies (Table SI-2).

425 *Model studies*. A second category of studies has applied models to interpret transfer from

426 plastic in a scenario analysis that includes all the other chemical uptake pathways (Figure 3)

427 as well.[24,25,26,28,75,76] These studies thus provide an environmentally relevant quantitative

428 assessment of the relative importance of plastic as a carrier of chemicals and have been

429 reviewed recently.[7,15] They combine empirically validated models for bioaccumulation from

430 regular prey with bioaccumulation from ingested plastic. Comparison of the HOC fluxes

431 bioaccumulated from ingested prey with those of ingested plastic, generally showed small to

432 negligible contributions of plastic to bioaccumulation by the various marine species like

433 lugworm, fish and seabirds.[25,26,28,75,76] These models accounted for cleaning effects due to

434 plastic ingestion,[24,25,26,28] were used for worst case scenarios setting the uptake from plastic at

435 maximum values (assuming 100% absorption),[28] or accounted for uncertainties in parameters

436 and input variables by using probabilistic approaches.[26] The main merit of these studies is that

437 they provide a mechanistic basis for understanding plastic-inclusive bioaccumulation, which

438 assists in data interpretation of empirical studies and experimental designs. Furthermore, they

439 allow for environmentally realistic scenario studies and extrapolations to low plastic

440 concentrations that occur in the environment, or to higher concentrations in the future. The

441 models that were applied are valid in terms of their agreement to first principles and

442 accordance with design criteria.[77] However, they can only provide indirect evidence, and lack

443 of validation against empirical data sometimes limits the credibility associated with these

444 modelling studies. We are aware of only two studies that compared model calculations with

445 empirical data,[25,75] which implies that further validation is recommended (see next section).

446 *Field studies*. A third category of studies proposes to use the observed co-occurrences or

447 correlations among field data on plastic densities or chemical concentrations in plastic, with

448 chemical concentrations in organisms, as evidence supporting the hypothesis of plastic

449 transferring HOCs to organisms.[38,78,79] The main merit of these field observations is that they

450 represent the ultimate reality of nature, which is the aim of this papers' research question. The

451 main challenge in observational field research, however, is proving causality because any

452 observed phenomenon can in theory be explained by many different mechanisms.[80] The

453 aforementioned correlations can be explained by several simultaneously acting processes, for

454 instance process 1 - 5 (Figure 3), or from any combination of these. The problem of multiple

455 causality through parallel uptake pathways means that it is difficult to unambiguously and

456 causally link bioaccumulation to ingestion of plastic alone. There is no reason to deny that

457 bioaccumulation of some HOCs can be linked to a high abundance of plastics that may act as

458 a source of these HOCs[38] (Figure 3, processes 3 and 5), however, the relative importance of

459 plastic *ingestion* is hard to disentangle. A final challenge associated with field studies is that if

460 statistical rigor is required, sufficient gradient in chemical concentrations, plastic abundance,

461 extent of plastic ingestion and mixing ratio with regular food is required. Such gradients are,

462 however, difficult to find on the scale of the oceans.[38]

463 We conclude that three categories of studies have discussed the role and importance of

464 microplastic ingestion. They seem to reach different conclusions because they address

465 different hypotheses, different exposure scenarios and have different limitations based on the

466 type of study (i.e. modelling, laboratory or field experiment), which are not always clearly

467 discussed. In summary; laboratory studies that use high doses of only plastic tend to find an

468 effect of ingestion on HOC accumulation. Studies aiming at environmentally realism (either

469 lab or model) by accounting for parallel uptake pathways tend to conclude that there is no (or

470 a negligible) effect. Field studies struggle with the problems of multiple causation, lack of

471 gradient and environmental variability, which limits their use to detect the contribution of

472 plastic ingestion to bioaccumulation.

473 **Unifying empirical studies, modelling studies, and theory.** To date, most model scenario

474 studies were prospective studies,[24,25,26,28] with only two studies also comparing model

475 simulation results with empirical data.[25,75] These scenario studies aimed at addressing

476 environmentally realistic settings by accounting for chemical bioaccumulation from water,

477 natural diet and ingested plastic. In this section we provide a synthesis of four categories of

478 information: (a) three published laboratory studies that provided evidence for transfer of

479 HOCs from microplastic to biota, (b) published model frameworks that include microplastic

480 as a component of the diet, (c) HOC release rate constants from microplastic measured under

481 gut mimicking conditions, and (d) theoretical estimations for these release rate constants

482 based on first principles. This way, the current model frameworks are further validated as they

483 are tested against published empirical data. The validity of the models was assessed based on

484 whether calibrated parameters align to independently measured parameter values, or whether

485 they agree to values that follow from first principles. In turn, inferences from empirical

486 studies that only addressed the release of HOCs from plastic in artificial gut fluids or that

487 applied plastic-only or plastic-dominated exposure conditions, can be and were extrapolated

488 to natural conditions by using the validated parameters. To that end, we parameterised a

489 previously published bioaccumulation model that includes plastic as one of the components in

490 the diet and that dynamically models HOC transfer in the gut[25] (provided as Supporting

491 Information, Table SI-3). The parameterisations and boundary conditions were set to match

492 the experimental designs and data from the studies by Browne et al[21], Rochman et al[66], and

493 Chua et al.[22] The main optimization parameter is the rate constant for chemical desorption

494 from plastic in the organisms' gut[15,25,27] (k_{1G}, d^{-1}, see previously published model provided as

495 Supporting Information), which also is the parameter providing the 'common currency' for

496 the four categories of information mentioned above. The calibrated k_{1G} parameters were

497 compared (a) with ranges for this parameter that were determined experimentally by Teuten *et*

498 *al*[12] and Bakir *et al*,[81] or recalculated from Tanaka *et al*[82] (see Table SI-4) and (b) with

499 parameter values inferred from first principles (i.e. plastic particles sizes and HOC intra-

500 polymer diffusivities). For the definition of the previously published model and its

501 parameters, and for the current new calculations the reader is referred to the Supporting

502 Information.

503 *Comparison of k_{1G} values estimated from modelling studies, bioaccumulation studies,*

504 *desorption studies and first principles.* Comparison of the magnitude of the rate constant for

505 desorption of HOCs from microplastics in the gut (k_{1G}) across different microplastic types and

506 sizes, organisms and chemicals, and obtained with different methods, has a range of about two

507 orders of magnitude (Table SI-5). The 10-90% inter quantile range $PR_{10-90\%}$ for the data in

508 Table SI-5, however, is only $0.3 - 9.8$ d^{-1} with a median of 2.1 d^{-1}. For the separate categories

509 of studies the median values as well as the $PR_{10-90\%}$ are virtually identical (Figure 4). This

510 implies that there is a striking consistency among the data obtained for these microplastics of

511 different sizes and polymer types, chemicals and methodologies. The estimates from

512 bioaccumulation studies, laboratory desorption studies and first principles provide very

513 similar ranges for the 'common currency' desorption rate parameter k_{1G}. For PAH desorbing

514 from PE and PVC the range is only about $1 - 4$ d^{-1} accounting for the bioaccumulation data

515 from Browne et al[21] and Rochman et al[66], the direct desorption measurements of Teuten et al[12]

516 and Bakir et al[81] as well as the theoretical values provided here (Table SI-5). The PCB k_{1G}

517 value estimated from the data provided by Rochman agrees well with values based on the

518 theoretical principles (Table SI-5).

519

520 **Summarizing Discussion**

The role of microplastic in the transport of HOCs. It has been shown that plastic is

ubiquitous in the marine environment.[3,4,7] Still, on average the present mass of plastic is

negligible compared to that of other media that transfers HOCs across the oceans. We applied

a 'back of the envelope' calculation that showed that on average the fraction of HOCs sorbed

by plastic also is negligible compared to the fraction held by other media (Fig. 2). The

fraction held by plastic is so small that even if we would underestimate the abundance of

plastic by orders of magnitude, plastic still would be unimportant as a transfer pathway for

HOCs. The same reasoning holds with respect to other uncertainties. The calculations used

here were based on the assumption of equilibrium partitioning for the main portion of

microplastic in the oceans. The outcome reflects the current state of plastic pollution in the

oceans, which may be valid for several more years. However, the yearly production of plastic

has increased over the years and can be expected to further increase. This implies that the

fraction of 'non-equilibrium plastic' will increase, and thus that the non-equilibrium fraction

will become increasingly important. Non-equilibrium may increase the potential role of

plastic as a carrier for additives and plasticizers, and decrease its role as a carrier for POPs.

Still, given the abundance of other media that carry the same chemicals, a substantial role of

plastic in the transport of chemicals is not likely.

The role of microplastic for the bioaccumulation of POPs, additives or plasticizers in the

marine environment. The previous sections provided evidence that showed transfer of HOCs

from plastic to organisms or vice versa, dependent on the fugacity gradient that was used in

the various study designs. We provided a synthesis that showed that laboratory exposure

studies, model studies and field studies all align and can be interpreted with existing theory of

bioaccumulation and partitioning of chemicals to hydrophobic phases such as sediment

organic matter and plastics. We demonstrated that the uptake of HOCs from plastics by

marine biota can be explained from the principles of polymer diffusion. In turn, the diffusion

546 rates explain the release rates observed in the desorption experiments,[12, 81] which in turn were

547 shown to be able to explain the observed bioaccumulation in experiments in which

548 uncontaminated test animals were fed contaminated plastic.[21,22] We showed that experiments

549 or field studies that also account for uptake from natural pathways are inherently less sensitive

550 to detect an effect of plastic, which simply represents the situation in nature and is explained

551 from the theory presented here. Indeed, parameters estimated from such an experiment[66] were

552 consistent with those obtained from laboratory desorption experiments and theoretical

553 principles. The above model calibrations and agreement of its parameters with values

554 independently obtained from experiments, further supports the credibility of the models that

555 have been used to infer the role of plastic as a carrier of HOCs to marine biota under natural

556 conditions.[24,25,28,75,76] Based on the synthesis we provided here, we suggest that the scientific

557 evidence is consistent, yet that the dichotomy in study outcomes is perceived and probably

558 reflects and is related to different exposure scenarios used in these different studies.

559 The central question we addressed is 'to what extent plastic ingestion leads to increased

560 uptake of chemicals in nature'. Here we briefly reflect on the studies that specifically aimed at

561 analysing such conditions, taking the aforementioned credibility of validated modelling

562 approaches into account. Gouin et al[24] used a model proposed by Arnot and Gobas[83] and

563 modelled HOC uptake from a 10% plastic diet. Such a percentage probably is very high for

564 the vast majority of marine organisms living in diverse habitats,[26,84] and instantaneous

565 equilibrium in the gut was assumed. This implies that a worst case was calculated, because

566 plastic might not fully equilibrate during gut passage. The biomagnification of HOCs was

567 calculated to decline up to 20% upon ingestion of plastic, for chemicals with a log K_{OW}

568 between 6.5 and 7.5. [24] In the laboratory, Rochman et al[66] exposed Medaka to a diet with 10%

569 plastic, and observed increased uptake of HOCs (ΣPAH) up to a factor 2.4. The 10% of

570 plastic in the diet as used in the studies by Gouin[24] and Rochman[66] is quite high compared to

571   conditions in many aquatic habitats[26] and thus can be considered to represent a (unrealistic)

572   worst case scenario. Besseling et al[74] investigated the effects of plastic ingestion on PCB

573   bioaccumulation by *A. marina*, taking all uptake pathways into account. A factor 1.3 increase

574   in bioaccumulation of ∑PCB was found, which however decreased with increasing plastic

575   concentration in the sediment. The increase was ascribed to physical effects of the plastic

576   ingestion and not to transfer of the chemicals from the plastic. Using the data from that study,

577   Koelmans et al[25] simulated the experiment and calculated a negligible contribution of plastic

578   in the transfer of PCBs compared to natural pathways. For an open ocean scenario, plastic was

579   calculated to attenuate biomagnification due to its fugacity being lower than that of biota

580   lipids. It was concluded that bioaccumulation due to ingestion by microplastic would be

581   negligible at plastic concentrations presently occurring in oceans sediments[25], a conclusion

582   that also was drawn for the modeled leaching of additives and subsequent uptake by

583   lugworms or cod.[26] In the previous section we showed that the parameters that were used in

584   these model studies align with values independently obtained from desorption studies, as well

585   as with values inferred from studies that only accounted for transfer from plastic. A fourth

586   model study was published recently by Bakir et al[28], who quantified the relative importance of

587   microplastics as a pathway for the transfer of HOCs to marine biota. First, the model was

588   validated using bioaccumulation data without plastic. Measured desorption rates (k_{1G}) from

589   plastics as in Table SI-5 were used and a plastic-inclusive model was implemented for

590   lugworm, fish and seabirds, with all uptake pathways accounted for. Their simulations

591   showed that plastic did not increase bioaccumulation for the lugworm, and decreased

592   bioaccumulation in fish and seabirds due to the 'cleaning' effect. However these differences

593   were marginal at the plastic concentration up to 5% dw of the diet. Only at a very high plastic

594   concentration of 50%, accumulation was predicted to increase (lugworm) or decrease (seabird

595   and fish), the latter decrease confirming the analyses by Gouin *et al.*[24] and Koelmans *et al.*[25]

596 We argue that these empirical laboratory studies and model studies agree that up to realistic as

597 well as at very high concentrations of about 1 to 10% of plastic in the sediment or in the diet,

598 about a factor two change of bioaccumulation in either direction may occur. It has been

599 argued recently, that the unrealistic high microplastic exposure concentrations as used in

600 many studies do not provide any information on the current risks to marine ecosystems.[85]

601 Instead, microplastic effect assessments should address more realistic i.e. lower and chronic

602 exposure conditions in sediments[85], as well as in the pelagic zone.[86] Under such more realistic

603 environmental conditions, organisms may simply ingest not enough microplastic particles

604 compared to natural prey, rendering the effect on bioaccumulation to be even below a 10-20%

605 difference in either direction.

606 As for field studies, we are not aware of reports that unambiguously quantify the quantity of

607 HOCs accumulated by marine aquatic organisms from ingested plastic, compared to natural

608 pathways. The variability in *in situ* bioaccumulation data has been analysed recently and was

609 shown to be between one to two orders of magnitude.[68] This implies that a factor of two

610 variation in either direction that can be seen under ideal conditions like in model studies or in

611 the laboratory, will be practically impossible to infer from field data. Effects of plastic

612 ingestion can be concluded to be smaller than the biological variability in bioaccumulation

613 data.[68] This implies that small effects of microplastic on bioaccumulation of HOCs can be

614 observed under artificial laboratory conditions, but in nature will be overwhelmed by natural

615 variability and by bioaccumulation from natural exposure routes.

616

617 **Implications for risk assessment**

618 Here we address the question whether microplastic ingestion leads to increased risks of

619 chemicals under realistic environmental conditions. The available data suggest that the effects

620 of microplastic ingestion on bioaccumulation probably stay within a factor of two, which is

621 within typical ranges of biological variability among individuals. For the majority of habitats,

622 bioaccumulation of HOCs from microplastic is probably overwhelmed by uptake via natural

623 pathways, a conclusion that also has been reached recently by the GESAMP WG40 working

624 group.[7] It has been argued that such a carrier effect of microplastic probably also is of limited

625 importance for the risk assessment of HOCs,[7,25] where assessment factors of 10 to 1000

626 usually are applied to account for variability and uncertainty in the effect assessment.

627 Furthermore, increased bioaccumulation or - magnification (including secondary poisoning)

628 only implies an increase in risk if the effect thresholds are exceeded, and such a formal risk

629 assessment to date has not been performed. To date, most studies aim at identifying a hazard

630 of microplastic ingestion by searching for potentially increased bioaccumulation. However, it

631 also has been argued[15] that microplastic ingestion may increase bioaccumulation for some

632 chemicals in the mixture (additives, plasticizers) yet decrease the body burden of other

633 chemicals at the same time (POPs), in case these chemicals have opposing fugacity gradients

634 between plastic and biota lipids.[24,25,28] For a balanced risk assessment aimed at protection of

635 populations or habitats, both effects should be considered, in relation to known effect

636 thresholds.

637 Our assessments used average and present oceanic conditions, which in reality will show

638 variation.[34] Given the high calculated factors between the current microplastic concentrations

639 and the microplastic concentrations required to cause an effect on chemical transport and

640 bioaccumulation, our assessment is rather robust with respect to such uncertainties. Still, risk

641 assessment should always consider local conditions where needed, and re-apply tests and

642 models for new cases. The same holds for prospective assessments that have to consider

643 increased emissions of plastic. Nanoplastic constitutes another uncertain factor, because the

644 abundance as well as the potential hazards of nanoplastic have not been addressed.[18,87] Our

645 suggestion that the effects of ingestion of microplastic on bioaccumulation most probably is

646 limited for most marine habitats and therefore hard to confirm by field data does not imply

647 that plastics do not have deleterious effects on marine life.[88] To answer this ultimate question,

648 more environmentally relevant, long-term effect studies with various species are needed.

649 **Acknowledgements**

653 **Supporting Information Available**

654 Text, figures and tables addressing the plastic-inclusive bioaccumulation model description,

655 model parameters, model simulation results. Modeling kinetic rate constants for desorption to

656 artificial gut fluids. Calculation of the distribution of HOC across environmental media.

657 Overview of studies that addressed the role of plastic in bioaccumulation of HOCs.

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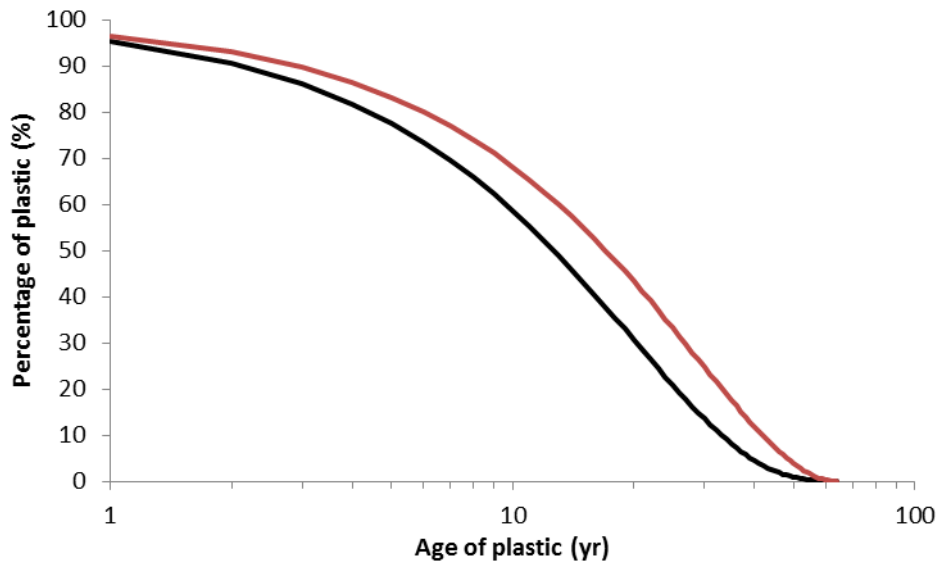
Figure 1. Cumulative age distribution of plastic in the oceans based on world plastic production data (━). For about 90% and 50% of the world-produced plastics, the residence time at sea is more than 2 y and 13 y, respectively. The red curve (━) represents the cumulative age distribution based on plastic production in Europe. Using the European production data, the 90% and 50% cut offs relate to residence times at sea of more than 3 y and 17 y, respectively.

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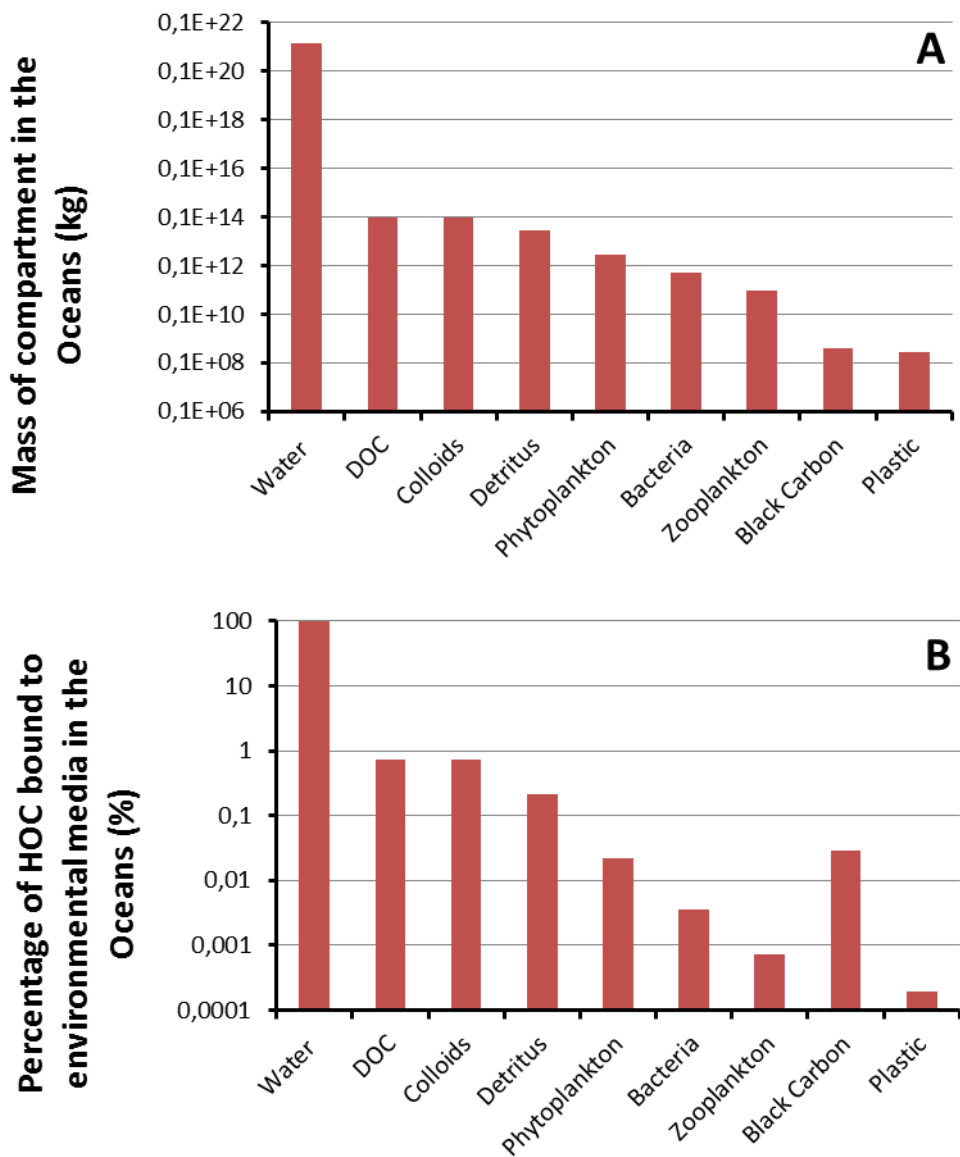
Figure 2. Abundances of environmental media in the oceans (Panel **A**), and distribution of HOC across these environmental media calculated using Equation 2 and 3 (Panel **B**). Water dominates the HOC distribution holding 98.3% of HOC whereas plastic holds 0.0002 % of HOC (Panel **B**). The calculations use highest reported K_P values for plastic and low estimated K_P values for organic carbon phases.
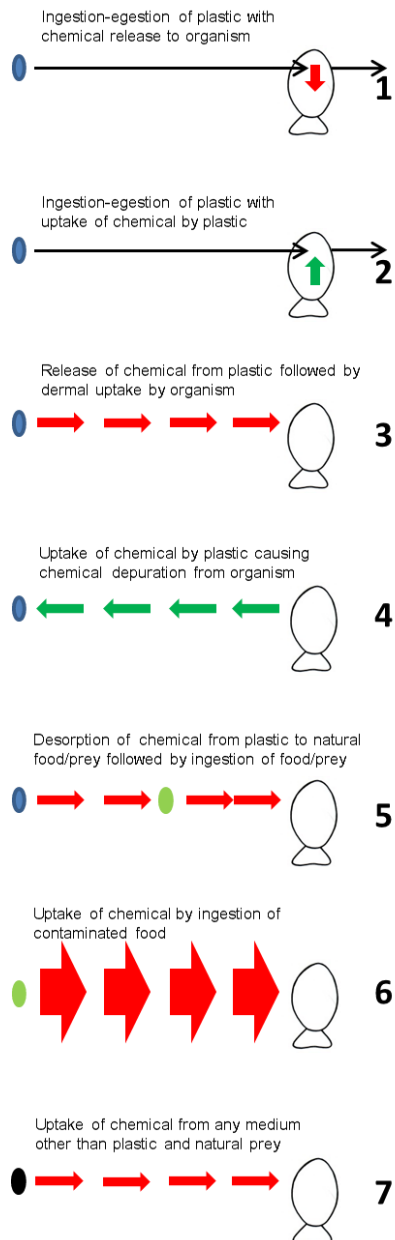
Figure 3. Simultaneous processes affecting the relative importance of microplastics acting as a vector of HOC to aquatic organisms, i.e. fish. ●=MP. ●=Natural prey item. ●=Other source than MP. Black arrows (→) indicate transfer of MP. Red arrows (➡) indicate HOC transfer to organism. Green arrows (⬅) indicate HOC transfer from organism. Arrow widths represent qualitative indication of relative importance of the pathway. Processes 1-5 involve a role of MP. Processes 5 and 6 involve natural uptake paths. Process 7 considers dermal exposure from other sources than MP. Per fish individual, processes occur simultaneously for same as well as different HOC, complicating interpretation of field data. Per fish individual, processes increasing or decreasing body burdens occur simultaneously for different HOC. Per HOC, uptake from natural path (6) plus non-MP source (7) generally overwhelms uptake from MP ingestion (1).
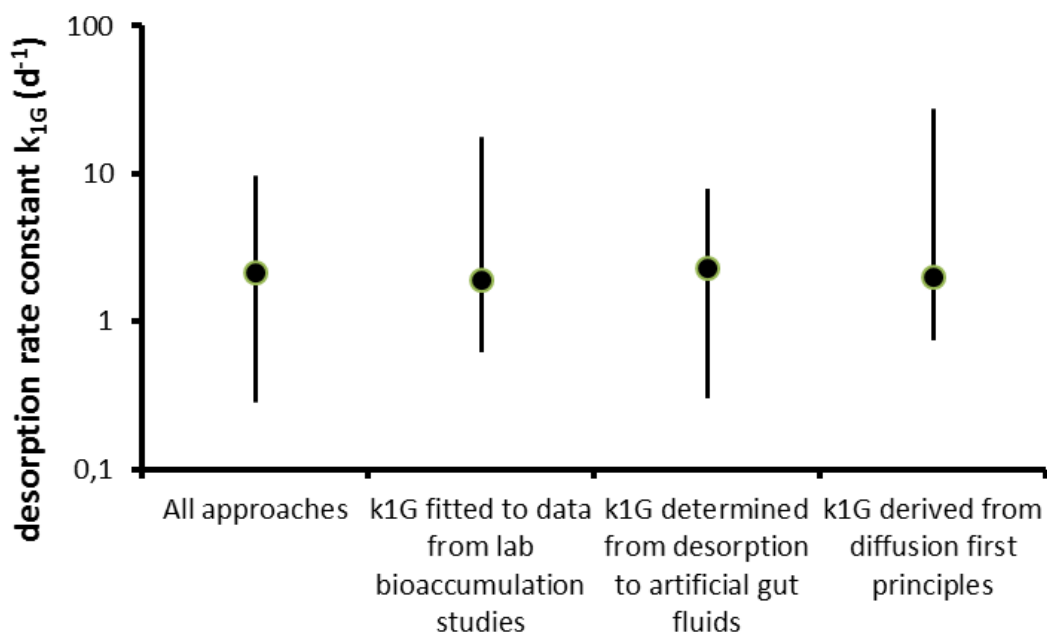
Figure 4. Similarity in median value and range (10-90% inter quantile ranges; $PR_{10-90\%}$) of
the rate constants (k_{1G}, d^{-1}) for desorption of HOC from plastic in the gut of marine biota, as
calculated using data from all study approaches, laboratory bioaccumulation studies,
desorption studies using artificial gut fluids, and diffusion principles. Detailed calculation of
the ranges is provided as Supporting Information.