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REVIEW ARTICLE

Spiking organic chemicals onto sediments for ecotoxicological analyses: an overview of methods and procedures

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Abstract

Laboratory testing with spiked sediments with organic contaminants is a valuable tool for ecotoxicologists to study specific processes such as effects of known concentrations of toxicants, interactions of the toxicants with sediment and biota, and uptake kinetics. Since spiking of the sediment may be performed by using different strategies, a plethora of procedures was proposed in the literature for spiking organic chemicals onto sediments to perform ecotoxicological analyses. In this paper, we reviewed the scientific literature intending to characterise the kind of substrates that were used for spiking (i.e. artificial or field-collected sediment), how the substrates were handled before spiking and amended with the organic chemical, how the spiked sediment was mixed to allow the homogenisation of the chemical on the substrate and finally how long the spiked sediment was allowed to equilibrate before testing. What emerged from this review is that the choice of the test species, the testing procedures and the physicochemical properties of the organic contaminant are the primary driving factors affecting the selection of substrate type, sediment handling procedures, solvent carrier and mixing method. Finally, we provide recommendations concerning storage and characterization of the substrate, equilibrium times and verification of both equilibration and homogeneity.

Keywords Ecotoxicology · Spiking · Labelling · Sediment · Organic chemicals · Bioaccumulation · Toxicity testing

Introduction

Organic contaminants are widely dispersed in most aquatic environments and represent a threat for biota at different trophic levels (Birch et al. 2018; Souza et al. 2018; Bignell et al. 2020). Toxicity testing and biomarkers are useful tools for characterising toxic effects due to exposure to environmental pollutants. Nonetheless, they provide aggregate information on the complex mixture of chemicals occurring in the sediments and do not allow to identify possible causality without any further investigation involving toxicity identification evaluation (TIE) or effect-directed analysis (EDA) (Burton and Nordstrom 2004; Li et al. 2019). Assessing effects on bulk-sediment basis is also considered the most variable approach to establish sediment quality criteria, due to the differences in contaminant bioavailability among sediments with different characteristics (Landrum et al. 1994; Hawthorne et al. 2006; Endo et al. 2020). Similarly, bioaccumulation studies on bulk sediment provide valuable data concerning exposure to pollutants and various processes that may enhance or mitigate bioaccumulation but have several drawbacks: Little information may be inferred concerning toxicokinetics ecotoxicity of single contaminants or groups of compounds (Weisbrod et al. 2009). These limitations constrain the development of suitable effect-level concentrations for organic chemicals based on bulk-sediment testing.

Spiking is defined as the experimental addition of chemicals, mixture, sludges, oils or even highly contaminated sediments to a control or reference sediment/soil to determine the toxicity and/or bioaccumulation of the added material (ASTM 1999; Northcott and Jones 2000). Laboratory testing with spiked sediments represents a valuable tool for ecotoxicologists: The semi-controlled conditions of the laboratory testing with substrates spiked with a known quantity of single toxicants allow researchers to study specific processes such as (1) effects of known concentrations of

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toxicants in single-species toxicity testing or manipulated ecology experiments, (2) interactions of the toxicants with sediment and biota, (3) uptake kinetics and transformation rates in sediments with different physicochemical properties and (4) advancement of the general understanding of benthic deposit-feeding ecology (US EPA 1992, 2001; Batley and Simpson 2016).

Spiked sediments have been widely used to derive effect-based quality criteria for polynuclear aromatic hydrocarbons (PAHs), organochlorine and pyrethroid pesticides (Swartz et al. 1990; Dewitt et al. 1992; Ankley et al. 1994; Amweg et al. 2005, 2006; Anderson et al. 2015) and biota-to-sediment accumulation factors (BSAFs) and critical body residues (CBR) (Landrum et al. 1994; Driscoll et al. 1997; Driscoll and Landrum 1997; Lotufo 1998a; Schuler et al. 2003). Spiked sediments have also been widely used for metals, to study concentration-effect relationship (Marasinghe Wadige et al. 2014; Wu et al. 2021) and bioaccumulation kinetics (Gimbert et al. 2016; Santana et al. 2017), and for evaluating the equilibrium partitioning theory based on the strong binding of sulphide in sediments (Simpson et al. 2004 and citation therein).

The addition of the organic chemical to the experimental system may be accomplished by using different strategies in several critical phases of the spiking procedure, including the preparation and manipulation of the substrate to be spiked, the introduction of chemicals to the prepared substrate and the mixing phase needed to distribute the chemical into the substrate homogeneously (Northcott and Jones 2000).

This paper provides an overview of the several methods developed by ecotoxicologists to create substrates to study the fate of organic chemicals in sediments, their accumulation and toxicokinetics and their toxicity towards the biota. Metals and other inorganic pollutants were not included in this review since their spiking onto sediments requires the adoption of materials and procedures different from those used for spiking sediments with hydrophobic organic chemicals. For example, spiking sediments with metals may require deoxygenated water and inert gases to minimise Eh and pH changes in the substrates or buffers to compensate for potential pH changes (Simpson et al. 2004). Furthermore, there is a vast literature on spiking sediments with metals and other inorganic chemicals that deserve an ad hoc review to be fully addressed and critically analysed.

In particular, our review aims to serve as a brief compendium for the identification of (1) which substrate may be used for spiking sediments with organic chemicals, (2) how it may be handled before spiking and then amended with organic chemicals, (3) how the spiked sediment may be mixed to allow the homogenisation of the chemical on the substrate and finally (4) how long it should equilibrate before testing. Finally, this review also provides recommendations to consider when setting up an ecotoxicological study on spiked sediments.

Data collection

We adopted a step-wise approach to identify the papers focusing on spiked sediments and ecotoxicology.

Firstly, Scopus® and Web of Science® (WoS®) were used as search engines to review the literature, using "sediment", "spiking", "spiked" and various synonyms of spiking as keywords. The complete list of the search queries typed in this phase is reported in Supplementary Material—Table S1. At this stage, we omitted to type keywords such as "ecotoxicology" and "toxicity testing" to avoid the use of too narrow search parameters. This first document search retrieved 899 papers with Scopus® and 453 with WoS®.

Secondly, we examined these papers to eliminate duplicate entries and select only the more relevant documents, reporting a detailed description of the spiking procedure and concerning the addition of organic compounds to reference or control sediments to perform bioaccumulation, biomarker or toxicity tests aiming to quantify effects and accumulation at predetermined nominal or actual concentrations. This screening procedure allowed to identify 201 research papers relevant for our review.

Thirdly, we examined the bibliography of these more relevant research articles to check for documents possibly missed by search engines. This further analysis provided a definitive list of 224 documents, covering over 30 years of ecotoxicological testing on spiked sediments (1981–2021). The complete list of the research articles taken into consideration for the present review is reported in Supplementary Material—Table S2.

Most of the research articles covered ecotoxicological analysis performed on freshwater species ($n = 138$), primarily toxicity testing and bioaccumulation. Information retrieved from each research article concerned the type of substrate (i.e. artificial or field-collected), handling procedures before spiking (i.e. sieving, freezing), spiking procedures, mixing method and equilibration time allowed to pass before testing. When available, also data on recovery, mixing efficiency (judged from coefficient of variations of sediment measured concentrations or deviations from mean value) and achievement of equilibration (judged from porewater concentrations) were retrieved.

Type of substrate

Based on information retrieved from the literature, the types of substrates used to create spiked sediments are four: field-collected sediments, artificial substrates (formulated

sediments), composite substrates and field-collected soils (Fig. 1).

Field-collected sediment is the substrate most often employed, both in freshwater ($n = 103$) and in marine/estuarine studies ($n = 81$). It is not surprising since the definition of spiking proposed by ASTM (1999) implies the use of "negative control or reference sediment/soil to determine the toxicity of the added material". Accordingly, natural sediments collected in pristine areas far from industrial pollution sources, characterised by absence of toxicity and contaminant concentrations' very low or below detection limits, were the substrate most often employed in spiking experiments aiming at quantifying the toxicity of added contaminants (Jeppe et al. 2017a, b; Nutile et al. 2017; Sinche et al. 2018; Chen et al. 2019). In some cases, the sediment collected in the test species collection site (native sediment) was employed as the substrate for spiking (Mulsow and Landrum 1995; Ciarelli et al. 1999; Peeters et al. 2000). In particular, native sediments have the advantage to allow exposing test organisms to optimal conditions as concern organic carbon content (TOC), grain size and food availability of appropriate quantity and quality. This property is critical, especially for long-term tests with growth rates as endpoints (Gunnarsson et al. 1999; Granberg and Forbes 2006).

Major disadvantages in using field-collected sediments rely on the varying physicochemical properties of natural sediments, primarily organic matter, that may affect the partitioning of organic chemicals. In particular, several studies

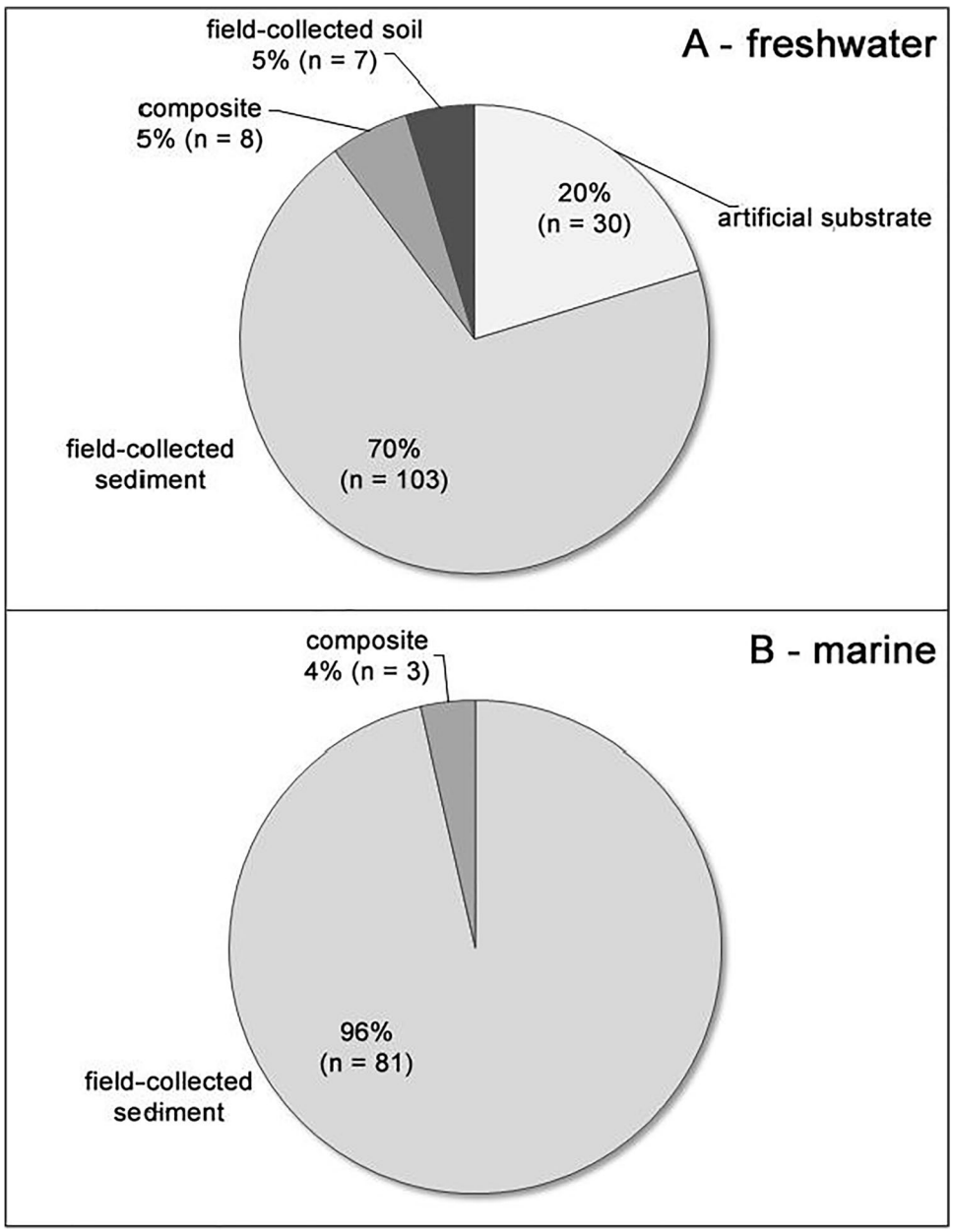


Fig. 1 Types of substrate used for preparing spiked sediment in aquatic studies

have evidenced the significant role of black carbon (BC) as a better adsorbent phase for organic pollutants as compared with other organic carbon sources in the sediments, including humic/fulvic substances, lipoproteins and lignin (Lohmann et al. 2005; Koelmans et al. 2006; Werner et al. 2010). Accordingly, the BC partition coefficients (K_{BC}) calculated for PAHs, polychlorinated biphenyls (PCBs) and other organochlorine pollutants are relevantly higher compared to the organic carbon partition coefficients (K_{OC}) usually used for predicting partitioning (Cornelissen et al. 2004; Lohmann et al. 2005; Koelmans et al. 2006; Zhang et al. 2008; Ali et al. 2016). Consequently, BC often resulted as the organic fraction controlling partitioning, bioaccumulation and toxicity of organic pollutants (Jonker et al. 2004; Sundelin et al. 2004; Koelmans et al. 2006; Sinche et al. 2018). As a result, even slight differences in the BC fraction (including soot, char and coals) may lead to sharp variations in the freely dissolved concentration (C_{free}) of a hydrophobic toxicant and complicate comparing the results among different tests and studies. Furthermore, the varying particle sizes of natural sediments may affect sorption and C_{free} of hydrophobic contaminants, leading to the differential distribution of the contaminants in the particle size fractions and differences in bioavailability (Kukkonen and Landrum 1996; Zhang et al. 2018).

When native sediments are not suitable for spiking, reference sediments may be prepared by blending two or more pristine sediments with different grain size and TOC (Call et al. 2001; Sormunen et al. 2009; Zhang et al. 2012; Martins et al. 2013, 2016). These composite substrates may represent a valid surrogate to native or natural sediments, but are an underexploited solution ($n = 11$) for both freshwater ($n = 8$) and marine environments ($n = 3$), although ASTM (2020) suggests that the substrate to be spiked may be prepared by manipulating the properties of control sediments.

In a limited number of studies with freshwater species ($n = 7$), field-collected soils, collected in pristine areas and slurried with reconstructed freshwater, were used as the substrate for spiking (Pagano et al. 2001; Schuler and Lydy 2001; Schuler et al. 2002, 2003; Ingersoll et al. 2005; Liu et al. 2015; Di et al. 2017).

A valuable alternative to field-collected sediments is an artificial substrate (formulated sediment). Artificial media constructed from commercially available components allow circumventing some uncertainties due to the varying physicochemical properties of natural sediments (Cui and Gan 2013). Furthermore, artificial substrates can be easily reproduced, prevent the cost of sampling large amounts of sediments, are free of contaminants and do not host indigenous organisms that may interfere with the test species (Fleming et al. 1998; US EPA 2001; Cui and Gan 2013). However, a major trade-off of using artificial substrates in bioaccumulation and toxicity testing is that they are often too simplistic to reproduce natural sediments' toxicity (Fleming et al. 1998; Åkerblom et al. 2008). Indeed, the carbon sources used for formulated sediments (including peat, α-cellulose and leaf material) are characterised by binding properties different from the complex organic matrix occurring in natural sediment (Hiki et al. 2021). Factors such as aromaticity, the extent of humification and BC content are usually higher in natural sediments than in formulated ones and may significantly affect the sorption of pyrethroids and PAHs (Cui and Gan 2013; Endo et al. 2020). Consequently, natural sediments tend to have a higher sorption capability than formulated sediment and result less toxic in spiked-sediment toxicity testing (Fleming et al. 1998; Åkerblom et al. 2008; Cui and Gan 2013). For example, studies on pyrethroids showed that K_{OC} and dissolved organic carbon partition coefficient (K_{DOC}) tend to be lower in leaf and cellulose-based artificial media than in natural sediments characterised by similar organic carbon contents (Fleming et al. 1998; Hiki et al. 2021). Consequently, lower K_{OC} values imply a higher aqueous phase concentration of chemicals, while lower K_{DOC} allows for increased exposure of the test species to the bioavailable fraction of the contaminant (Cui and Gan 2013). Furthermore, the lack of biological activity and oxidation–reduction potential gradients in formulated sediments undoubtedly alters some sorption and desorption properties, which might in turn alter contaminant fate and effects (US EPA 2001).

The use of artificial substrates, although quite diffused, was restricted to freshwater studies ($n = 30$). The availability of formulations for freshwater sediments proposed by several authors (Naylor and Rodrigues 1995; Suedel and Rodgers 1996; Harrahy and Clements 1997; Kemble et al. 1999) and international organisations (OECD 2004, 2007; ISO 2010) may have favoured the use of artificial substrates in spiked-sediment studies involving freshwater species such as oligochaetes, chironomids and nematodes (Egeler et al. 2001, 2010; Oetken et al. 2005; Jungmann et al. 2009; Groh et al. 2010; Bettinetti et al. 2018; Höss et al. 2020). Conversely, the lack of guidelines and the scant literature concerning artificial marine sediments (Walsh et al. 1990) may have contributed to addressing the research to field-collected sediments, as a substrate for spiking. Besides the possible overestimation of the toxicity due to the lower binding properties of artificial substrates as compared with natural ones, major disadvantages that may have discouraged the use of artificial substrate for marine testing also include costs and time needed to prepare large volumes of material to be spiked, and the difficulty to reproduce optimal condition for the test species in terms of TOC, grain size and food availability.

Sediment manipulation before spiking

In general, the manipulation of the sediment before the addition of the chemical is probably not critical for spiking studies whose purpose is to identify effective concentrations or critical body residues, since the spiking procedure itself provides for the vigorous mixing of the substrate to obtain a homogeneous distribution of the contaminant within the sediment/soil. Furthermore, manipulations are necessary for the sediment's storage and transport and testing the spiked substrate with benthic species (i.e. sieving).

Inevitably, however, removing sediments from their natural environment causes changes as the substrate detaches itself from its natural conditions. Sediment environments are composed of many of microenvironments, redox gradients and other interacting physicochemical and biological processes, and many of these features influence sediment toxicity and bioavailability to sediment flora and fauna, microbial degradation and chemical sorption (Burton 1992). Consequently, any disruption of this environment complicates the interpretation of treatment effects, causative factors and in situ comparisons. Any method employed to add organic contaminants to soil and sediment will be a trade-off between the requirements of the experiment and the practicality of limiting changes to the substrate (Burton 1992; Northcott and Jones 2000). Interferences that can affect solubility and partitioning of chemicals may be introduced by storing sediments at temperatures other than field conditions, changing the moisture of the sediment, photolysis and materials used in the experiment (Northcott and Jones 2000). The adopted spiking might also introduce artefacts that may complicate the interpretations of the results; however, little information is available on spiking procedures' effects on experiments (Northcott and Jones 2000).

Adopting procedures that minimise the substrate's manipulation is necessary to limit changes to the physicochemical properties of the sediments that may alter the organic compound's chemical sorption on the substrate, its bioavailability and its toxicity. In particular, Northcott and Jones (2000) identified sample storage, drying/rewetting and sieving as manipulations that should be carefully considered for a spiking procedure, because they may introduce significant changes to the physical, chemical and biological features of the sediment/soil. In facts, the disruption of substrate's microenvironments by keeping it at a temperature other than field conditions, changing the moisture content or its sediment/water ratio and storing it at conditions that promote degradation (i.e. photolysis, ammonia and sulphide build-up) may severely complicate the interpretation of treatment effects, causative factors and in situ comparisons.

For storage, refrigeration at 4 °C is the recommended method, since it allows minimising both biological and chemical degradation processes and changes in pollutant bioavailability (Northcott and Jones 2000; ASTM 2020). Conversely, freezing the samples is not recommended, since it may affect the toxicity of sediments spiked with organic compounds (Schuytema et al. 1989; Day et al. 1995), change physicochemical appearance and properties of the sediment (Schuytema et al. 1989; ASTM 2020) and increase the C_{free} of organic contaminants as compared with freshly collected sediments (Jonker 2021). Storage conditions before spiking are clearly stated only in a limited number of research papers. We retrieved information concerning storage temperature only from 97 out of 224 research articles (43%) and observed that cold storage at temperatures in the range 0–5 °C is the more diffusely adopted approach ($n = 81$). In a few cases, sediments were stored frozen, at temperatures ranging from − 80 °C up to − 18 °C ($n = 18$); according to the authors, freezing was accomplished to eliminate indigenous fauna (Higgins et al. 2007; Paumen et al. 2008; Brock et al. 2016) or to store previously freeze-dried sediments (Barjhoux et al. 2014; Creusot et al. 2016). Storage time is often undefined, since most of the examined papers report that sediments and soils were cold-stored or frozen "until spiking", "until use" or "until dosing" without any specification of the period ($n = 195$). When storage time is stated, it is reported to range from 1 day (Kheir et al. 2001; Jeppe et al. 2017a) up to 1 year (Droge et al. 2008), with most authors reporting a cold storage up to a few weeks (Nipper et al. 2005; Rosen and Lotufo 2005; Åkerblom et al. 2008; Rico-Rico et al. 2009; Mauffret et al. 2010a, b).

Sieving can affect bioavailability and accumulation by changing the particle size distribution and decreasing TOC content, therefore affecting the uptake of sediment-bound organic contaminants to size-selective suspension and deposit feeders (Kukkonen and Landrum 1995; Northcott and Jones 2000; US EPA 2001). However, sieving field-collected sediment is often necessary to remove debris and indigenous fauna which may interfere with toxicity due to similarity in shape and size with the test species, possible predation on test organisms and competition for organic carbon sources (US EPA 2001). When sieving is necessary to remove indigenous fauna, it should be performed by press sieving the sediment through a 1-mm or 2-mm mesh size screen (ASTM, 2020). Wet sieving, namely the swirling of sediment particles using water to facilitate the separation on the sieve, should be avoided unless it is necessary for specific purposes, i.e. testing the effect of grain size and organic matter on toxicant partitioning (Swartz et al. 1990), and also in these cases it should be performed by using as small volume of water as possible.

Our review retrieved information on sieving from 127 papers and evidenced the use of substantially varying mesh sizes for screening sediments. The most often employed

mesh sizes are 500 µm, 1 mm and 2 mm, but a relevant number of papers reported the use of sieves with mesh sizes < 250 µm and > 2 mm (Fig. 2). The size of test species serves as the main factor conveying the choice of the sieve's mesh: A sieve with a mesh size larger than 1000 µm is appropriate for removing macrobenthic invertebrates from field-collected sediments, but it is too wide to hold small polychaetes (Spionidae and Capitellidae) and meiofauna such as benthic copepods (Fig. 3). Test with harpacticoids and spionids generally implied the use of screens with mesh size < 250 µm (Green and Chandler 1996; Ferguson and Chandler 1998; Lotufo 1998b; Chandler and Green 2001), even if some authors also used larger screens (Nipper et al. 2005), while testing with oligochaetes, marine amphipods and large polychaetes such as Nereididae allowed for the use of sieves with mesh size > 250 µm. Press sieving was the most applied techniques, and wet sieving was applied only in a limited number of cases (Murdoch et al. 1997; Bettinetti et al. 2002; Bettinetti and Provini 2002; Higgins et al. 2009; Milani et al. 2018).

Drying of sediments is seldom used before spiking to decrease the variability of their inherent heterogeneity, to ease their handling and processing by removing agglomerates and to improve sample mixing efficiency and spike distribution onto substrates (Díaz-Jaramillo et al. 2016). Some authors dried sediment also to reduce possible interferences due to volatile organic compounds (Maranho et al. 2015b; Pusceddu et al. 2018). Drying, however, cause significant

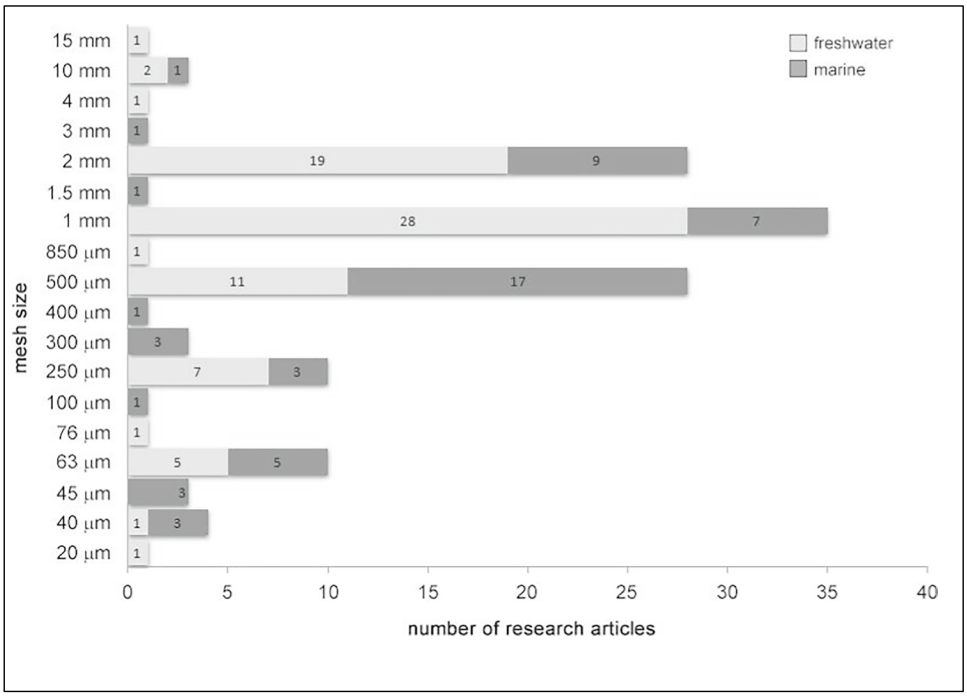


Fig. 2 Mesh size used for screening field-collected freshwater and marine sediments before spiking with organic chemicals

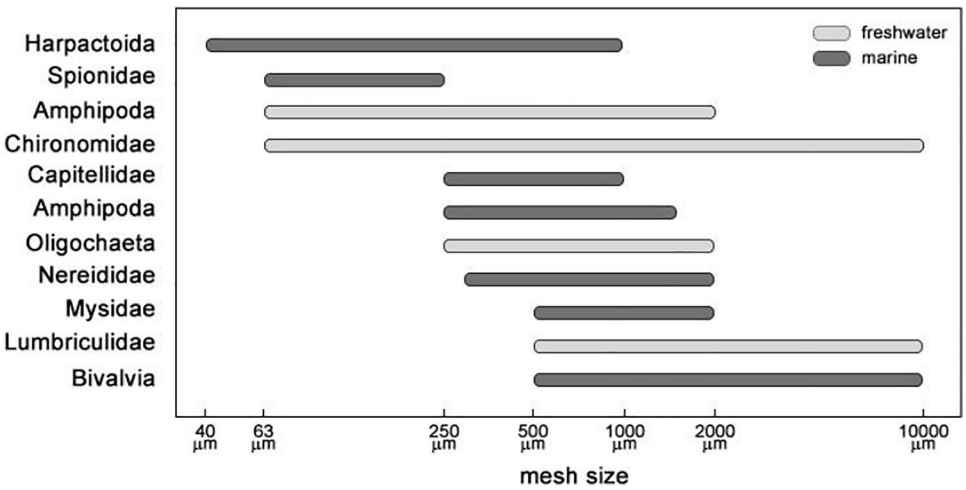


Fig. 3 Ranges of mesh size used to separate indigenous fauna from field-collected sediments before spiking sediment for testing with marine and freshwater invertebrates. *Y*-axis reports the main invertebrate taxa used for toxicity testing or bioaccumulation experiment with spiked sediments; *X*-axis reports sieve mesh sizes on a logarithmic scale

modifications in the chemical and physical properties of soils and sediments (including aggregate stability, distribution of organic matter, flush of nutrients) and these changes also extend during the dry storage (Northcott and Jones 2000). The most exploited drying techniques were air-drying the sediment for several days ($n=10$) or drying it in the oven ($n=9$) at temperatures ranging from 60 °C (Méndez et al. 2013) up to 105 °C (Conder et al. 2004). The rewetting of dried sediment before spiking was performed in a limited number of studies, by adding the same amount of water lost after drying (Ingersoll et al. 2005; Balthis et al. 2010; Maranho et al. 2014, 2015a, b; Pusceddu et al. 2018).

Before-spiking manipulations less frequently used included freeze-drying ($n=7$), autoclaving the sediments ($n=6$) and gamma irradiation ($n=1$). Freeze-drying the sediment before storage was an alternative approach to air-drying; it was proposed by some authors for testing freshwater spiked sediment with fishes, *Daphnia magna* and in vitro tests (Zhou and Wong 2000; Vicquelin et al. 2011; Feo et al. 2013; Barjhoux et al. 2014; Vignet et al. 2014; Creusot et al. 2016). Autoclaving field-collected sediment was performed to sterilise the substrate before creating a slurry to be spiked with organics for testing with marine meiofauna (Green and Chandler 1996; Lotufo, 1997, Lotufo, 1998b; Ferguson and Chandler 1998; Chandler and Green 2001). Gamma irradiation is an alternative to freezing to remove metazoa (Millward et al. 2001).

Spiking procedures

The goal of most spiking studies is to determine the effects of the spiked chemical. The results of such studies can be used to interpret data from field samples, and help determine the causes of toxicity or other effects. Spiking sediments is a procedure that involves different actions: the selection of the compound for spiking, the preparation of a spiking solution using an appropriate solvent, the addition of the spiking solution to the sediment/soil, the mixing of the spiked substrate to obtain a homogeneous sample and the equilibration phase needed to allow contaminant partitioning within the sample matrix. Since each one of these actions may be performed following different methods, several distinct spiking procedures were proposed in the literature for the study of both effects and bioaccumulation of organic pollutants.

Types of spiking compounds

Different types of organic chemicals were used to spike artificial and field-collected sediments, including native compounds, radioactively labelled compounds, mixtures of native and labelled compounds and commercial products/mixtures.

Analytical reagent-grade native standards are the most employed compounds for spiking sediments and soils ($n=173$), since they can be easily purchased from different science and biotechnology companies as compounds of known purity and enantiometric composition. Radioactively labelled compounds, alone ($n=24$) or as a mixture with native compounds ($n=21$), were used primarily in studies aiming to assess uptake, metabolism and bioaccumulation of aromatic hydrocarbons (PAHs) and organochlorine compounds in benthic deposit feeders (Varanasi et al. 1985; Landrum et al. 1994; Lotufo et al. 2001c; Selck et al. 2003), even if experiments with linear alkylbenzene sulphonates (LAS), phthalates, cyclonitrammine compounds and pesticides were reported too (Call et al. 2001; Lotufo et al. 2001b; Comber et al. 2006; Maul et al. 2008; Ding et al. 2013). In such studies, radioactively labelled standards offer the advantage over native standards of allowing the measure of low concentration of organic chemicals into small volumes of porewater, sediment and organic tissue by using liquid scintillation counting of radioactive product decay (Word et al. 1987). Commercial mixtures were used in a limited number of cases for pesticides (Van Geest et al. 2014; Brock et al. 2016, 2018; Mehler et al. 2017), polybrominated diphenyl ethers (Klosterhaus and Baker 2010; Klosterhaus et al. 2011) and phthalates (Call et al. 2001). Commercial formulations of pesticides and herbicides are usually available as water-soluble mixtures; therefore, organic solvents for the solubilization of the active ingredient before spiking are not required (Van Geest et al. 2014; Brock et al. 2016, 2018; Mehler et al. 2017). On the other hand, purity and composition of commercial products have to be analytically verified, both to assess the purity of the active ingredient and the occurrence of potentially toxic excipients.

Solvent carrier

According to Northcott and Jones (2000), water is the ideal solvent to add a chemical to sediments or soils; nevertheless, the authors acknowledged that water solubility of many hydrophobic contaminants is too low to obtain concentrated aqueous solutions suitable for spiking. As a consequence, a spiking solution in distilled water or seawater was prepared exclusively for compounds such as commercial formulations of pyrethroid pesticides, LAS, explosives and related compounds, and some pharmaceuticals (Nipper et al. 2004, 2005; Péry et al. 2008; Mauffret et al. 2010a, b; Teodorović et al. 2012; Van Geest et al. 2014).

Primary factors driving the choice of the more suitable organic solvent for hydrophobic organic contaminants are the solubility of the contaminant in the candidate solvent, the toxicity of the solvent towards the test species and its persistence in the substrate (Northcott and Jones 2000; U.S. EPA 2002). Our review indicated that acetone was

the most employed solvent carrier; it was used mostly as pure chemical, but in some cases also in mixtures with other organic carriers, including methanol, toluene, dimethyl sulphoxide (DMSO) and n-hexane (Fig. 4). Other organic solvents commonly used are methanol (MET), hexane (including *n*-hexane, *iso*-hexane and cyclohexane) and DMSO. Solvent carriers such as toluene (TOL), pentane (PEN), ethyl acetate (EA) and dimethylformamide (DMF) were used only in specific treatments for PBDEs, decamethylcyclopentasiloxane and organochlorine pesticides (Nebeker et al. 1989; Schuytema et al. 1989, 1990; Klosterhaus and Baker 2010; Klosterhaus et al. 2011; Norwood et al. 2013). None of the selected papers reported the use of ethanol.

When a solvent carrier is used, a solvent blank (or solvent control) is usually performed to test for possible solvent-induced effects ($n = 178$). Solvent blanks are prepared by adding to uncontaminated substrates an equivalent volume of solvent, as in the treatments.

Addition of the spiking solution

Based on the description reported in the original papers, the various spiking methods may be grouped into five distinct categories, as outlined below.

- **Conventional sediment spiking method**. It is the easiest and fastest method: The chemical is directly added to the substrate by adding an appropriate volume of the chemical/solvent-carrier solution directly on the substrate surface during or followed by thoroughly mixing. The USEPA (2002) does not recommend this method when using solvent carriers, since they might alter sediment chemistry, including toxicant bioavailability. Northcott and Jones (2000) remarked that the addition of the spiking solution to the substrate could be performed by using low or high solvent volumes. Accordingly, low solvent volume methods imply the use of a solvent to solid ratio of 1:20 (volume:weight) or greater, while procedures

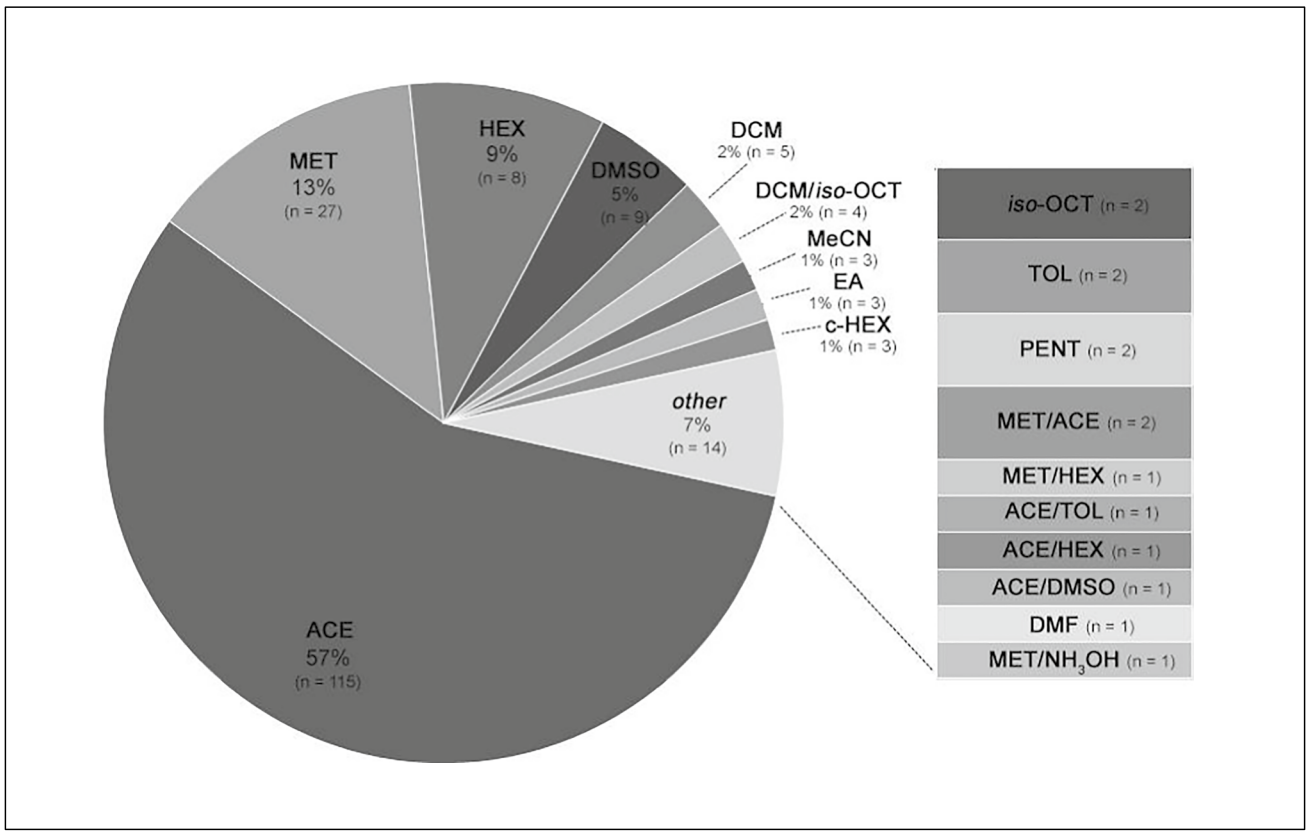


Fig. 4 Solvent carriers used for spiking organic chemicals into sediments. ACE = acetone; MET = methanol; DMSO = dimethylsulphoxide; HEX = sum of *n*-hexane and *iso*-hexane; DCM/*iso*-OCT = mixture of dichloromethane and *iso*-octane; DCM = dichloromethane; MeCN = acetonitrile; EA = ethyl acetate; c-HEX = cyclohexane; *iso*-OCT = iso-octane; TOL = toluene; PENT = pentane and *n*-pentane; MET/ACE = mixture of methanol and acetone (1:1); MET/HEX = mixture of methanol and hexane; ACE/TOL = toluene 5% solution in acetone; ACE/HEX = mixture of acetone and hexane (1:3); ACE/DMSO = mixture of acetone and DMSO (10:1); MET/NH_3OH = 0.01% ammonium hydroxide solution in methanol; DMF = dimethylformamide

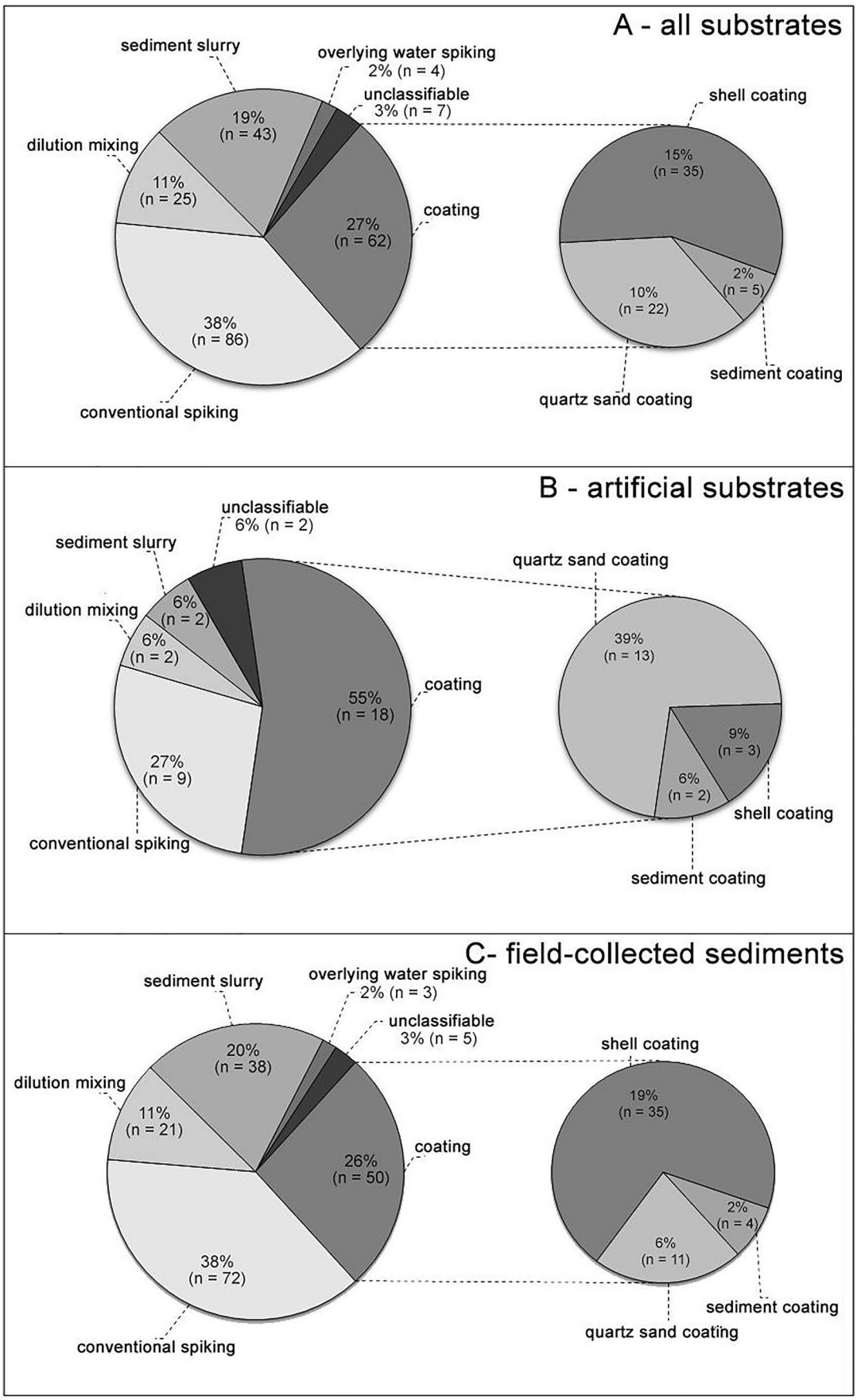
using a ratio < 1:20 are referred to as high solvent volume methods. The use of high volumes of solvent can lead to the extraction of labile components and alter the natural distribution of organic matter within the soil and sediments. Thus, the volumes of the carrier solvent must be minimised because they have the potential to alter the OC concentration in the interstitial water of the sediments, the solubility of the compounds and the partitioning behaviour due to the cosolvent effect. Furthermore, the excess volume of solvent can cause specific reactions of organic compounds in the soil by mobilising the reactants and increasing the reaction rates. Nevertheless, solvent-carrier volumes are often not reported in the papers, making this distinction not functional for this review.

- **Dilution mixing method**. In the dilution mixing, a small aliquot of the substrate, both dry and wet, is spiked to a high concentration of toxicant by adding an adequate volume of chemical/solvent-carrier solution and then thoroughly mixed (Barber et al. 1997, 1998). This high concentration matrix, also called "super-spike" (Mehler et al. 2018), is allowed to equilibrate under a fume hood to facilitate the evaporation of the solvent carrier, and then blended or mixed with uncontaminated substrates to obtain the desired volume of toxicant concentrations. The high concentration matrix is often prepared by using 10% of the sediment to be spiked, for not only both artificial and field-collected substrates (Barber et al. 1997, 1998; Zielke et al. 2011; Cofalla et al. 2012; Brinkmann et al. 2013), but also smaller amount. Dilution mixing of the high concentration matrix with the remaining uncontaminated substrate reduces the residual concentration of solvents in the final testing sediment/soil substrate, minimising the risk of false-positive responses due to biota-solvent interaction in toxicity tests.
- **Coating methods**. The coating technique is an elaborated procedure that relies on the generation of a crystalline or liquid deposit of toxicant on the interior surface of glass vessels or small aliquots of a substrate. In the shell coating technique, appropriate volumes of the spiking solution are added to open-top glass containers; then, the solvent carrier is allowed to evaporate creating a crystalline deposit of toxicant on interior surfaces of the glass vessel (Schuytema et al. 1988, 1989; Ditsworth et al. 1990). Alternatively, a small quantity (i.e. 10 g) of dried quartz sand or sediment can be added in the glass containers, to allow for the "coating" of the quartz sand or sediment rather than of internal walls of the vessel (Egeler et al. 1997; OECD 2004; Bolyard et al. 2017). Once the solvent carrier has entirely evaporated, the bulk wet sediment is added to the vessel and mixed by rolling (to abrade toxicants from walls) or stirring. Small amounts of water (i.e. 50 mL) may also be added to increase substrate fluidity, prevent tumbling and facilitate the mixing (Ditsworth et al. 1990). Shell coating is the method suggested by the USEPA (2002) to minimise the risks associated with the use of solvent carriers. Although toxicant's evaporation is not reported as a possible consequence of the shell coating procedure, care should be taken when using rotary evaporators or other devices intended to allow the rapid evaporation of the solvent, since also toxicants may be lost during this phase.
- **Sediment slurry method**. This method relies on the production of a fluid slurry before or during the spiking procedure. This procedure may be accomplished either by adding the spiking solution to the substrate via a carrier solvent immediately followed by addition of uncontaminated water and mixing, or by adding the toxicant to a slurry obtained by mixing the substrate with uncontaminated natural or reconstructed water and subsequent mixing (Loonen et al. 1997; Northcott and Jones 2000; U.S. EPA 2002). After mixing, the excess of water has to be removed by centrifugation or aspiration. The essential assumption of the method is that the solvent is removed during the mixing/stirring phase or by the centrifugation/aspiration of the overlying water. The sediment to water ratio used to slurry the sediment vary widely among studies (see Supplementary Material).
- **Overlying water spiking**. This method implies the addition of the chemical(s) to the water overlying the sediment rather than into sediments. It is designed to reflect field conditions where inputs of the chemical occur via water (treated or untreated discharges or atmospheric depositions). The method is best applied to organics with high water solubility (Van Geest et al. 2014) or to organics dissolved into a water-miscible solvent, such as acetone (Northcott and Jones 2000; Gomiero et al. 2018).

We further introduced the category "unclassifiable" to include all methods that were not exhaustively described and thus not classifiable within the categories mentioned above.

The literature review underlined that conventional sediment spiking is the most often employed method, followed by coating techniques (Fig. 5A). Differences in the choice of spiking methods between artificial and field-collected sediments are quite relevant: Conventional spiking is the preferred method for spiking field-collected sediments with organics (Fig. 5C), while quartz sand coating is the most often used methods for artificial substrates (Fig. 5B). Sediment slurry and dilution mixing methods are widely applied to field-collected sediments but only occasionally to artificial substrates, while overlying water spiking is limited to few studies on field-collected sediments (Fig. 5B and Fig. 5C).

As noted by Northcott and Jones (2000), the method used for spiking may be in some cases determined by the experimental conditions, the nature of the substrate and the degree to which it can be manipulated. However, since


A - all substrates
sediment slurry
overlying water spiking
2% (n = 4)
unclassifiable
3% (n = 7)
shell coating
19%
(n = 43)
dilution mixing
11%
(n = 25)
coating
27%
(n = 62)
15%
(n = 35)
2%
(n = 5)
10%
(n = 22)
38%
(n = 86)
sediment coating
conventional spiking
quartz sand coating
B - artificial substrates
unclassifiable
6% (n = 2)
sediment slurry
quartz sand coating
dilution mixing
6%
(n = 2)
6%
(n = 2)
coating
55%
(n = 18)
39%
(n = 13)
9%
(n = 3)
6%
(n = 2)
27%
(n = 9)
shell coating
conventional spiking
sediment coating
C- field-collected sediments
sediment slurry
overlying water spiking
2% (n = 3)
unclassifiable
3% (n = 5)
shell coating
20%
(n = 38)
dilution mixing
11%
(n = 21)
coating
26%
(n = 50)
19%
(n = 35)
2%
(n = 4)
6%
(n = 11)
38%
(n = 72)
sediment coating
conventional spiking
quartz sand coating

◂**Fig. 5** Spiking methods employed for adding the spiking solution to the substrates. In panel **A**, data are reported by pooling the type of substrate (artificial substrate, field-collected sediment, composite and field-collected soil). Panel **B** shows methods used for spiking artificial substrates, while panel **C** reports the methods used for field-collected sediments

the composition of formulated sediments may be adjusted to the purpose of the study, the substrate's characteristics may represent a limit for selecting the spiking procedure only for field-collected sediments and soils. For example, muddy and water-saturated substrates may be spiked using the overlying water spiking, the sediment slurry method or any coating techniques with minimal disturbance of their physicochemical properties. Conversely, natural silty and clayey sediments may be hardly spiked using the sediment slurry method and coating techniques without the addition of water, with consequent changes of their natural moisture and cohesiveness.

Mixing method and mixing times

The purpose of mixing is to obtain a homogeneous distribution of the contaminant within the substrate, to assure replicability and statistical validity of the experimental data and avoid high variability of the results. Thus, regardless of the spiking method used, care should be taken to ensure complete and homogenous mixing (U.S. EPA 2002).

Mixing can be performed by hand or by using different mechanical devices allowing for the stirring of the substrate or the shaking, rolling and rotation of the glass containers. Based on the type of device and mixing technique described in the papers, we broadly classified the reported mixing methods into five categories.

- **Mechanical stirring**. In the "mechanical stirring" category, we included all methods that allow the mixing of the spiked sediment/slurry by blending it a circular pattern. Stirring implies the contact between the spiked sediment/slurry and mechanical parts of the devices; these latter should consist of stainless-steel paddles or Teflon-coated stirring magnets to avoid contamination of the sample and sorption/desorption of organic contaminants. Several different motor stirrer laboratory devices are used to achieve the mixing, including magnetic stir plates (Green and Chandler 1996; Nipper et al. 2002; Brils et al. 2002; Conder et al. 2004; Eriksson Wiklund et al. 2009), impeller mixers and drills equipped with rotating paddles (Lotufo et al. 2000, 2001a; Schuler et al. 2003; Croce et al. 2005; Rosen and Lotufo 2005; You et al. 2006; Sormunen et al. 2008, 2009). Other non-laboratory instrumentation employed for stirring are concrete (Hutchinson et al. 2003; Cofalla et al. 2012; Höss et al. 2020) and stand mixers (Kheir et al. 2001; Daoud et al. 2018). Most of the procedures proposed mixing times ranging from a few minutes up to 24 h, with most of the paper reporting a mixing time in the range 2–24 h and only a few research articles prolonging the mixing over 7 days (Tian and Zhu 2011; Tian et al. 2012; Dang et al. 2016).
- **Mechanical shaking**. This category includes all the procedures allowing for the mixing by moving backwards/forwards or up/down the glass container, while the spiked sediment/slurry does not enter in contact with the mechanical parts of the device. The most often employed laboratory tools are rotary shakers (Casellato et al. 1992; Cachot et al. 2007; Gilroy et al. 2012), reciprocating shakers (Van Geest et al. 2014), wrist-action shakers (Plesha et al. 1988) and orbital mixers (Fay et al. 2000; Higgins et al. 2009; Stringer et al. 2014). For small volumes of sediment, vortexing is a cost-effective and incisive solution (Chandler and Green 2001; Lam et al. 2010). Rotary evaporators have also been successfully used for the simultaneous solvent evaporation and mixing of small volumes of sediment for testing with fishes (Vicquelin et al. 2011; Barjhoux et al. 2014; Le Bihanic et al. 2014a, b). Non-conventional instrumentation successfully used for mixing spiked sediment includes also paint can shakers (Raimondo et al. 2014). Mechanical shaking is usually performed for a time ranging from a few minutes up to 1 day, although longer mixing times have been often proposed, up to several weeks (Schuytema et al. 1990; Zhou and Wong 2000).
- **Sediment rolling**. Ditsworth et al. (1990) proposed the rolling of cylindrical vessels containing the spiked substrate as an ideal mixing method to follow the coating of vessels with the toxicant. By using a rolling mill or a similar apparatus, mixing is achieved gravimetrically by slowly rolling the vessels, usually at speeds not exceeding 15 rpm (Bell et al. 2004; Ingersoll et al. 2005; Nipper et al. 2005; Ratier et al. 2019). Dilution water may be added to the spiked sediment before rolling, to achieve a sediment-to-water ratio optimal for mixing and facilitating the abrasion of toxicants from vessel's walls (Murdoch et al. 1997; Ciarelli et al. 1999; Péry et al. 2003; Rust et al. 2004; Ingersoll et al. 2005). According to the USEPA (2002), the sediment rolling method is the more suitable methods for spiking larger volumes of sediments. The USEPA (2002) recommended rolling of the spiked substrate for greater than 2 h to achieve sample homogeneity, with the advice to avoid prolonged rolling times (> 1 week) to minimise changes in physicochemical properties. Most of the researchers followed these recommendations, with a few exceptions providing for rolling for more than 10 days (Boese et al. 1990; Hoke

et al. 1995; Kosian et al. 1999; Millward et al. 2001; Bell et al. 2004) or less than 1 h (Pusceddu et al. 2018).

- **Rotatory mixing**. In the rotatory mixing, the vessels containing the spiked sediment or slurry are rotated end-to-end to facilitate the homogenisation, by using overhead mixers, tumblers or rotational shakers (Chai et al. 2007, 2008; Milani et al. 2018). This technique is an alternative to sediment rolling for large volumes of substrates, since overhead mixers and tumblers allow for the simultaneous mixing of several vessels with over 1 L of capacity. Rotatory mixing was performed for a minimum of 2 h (Balthis et al. 2010; Milani et al. 2018) up to a maximum of 20 days (Díaz-Jaramillo et al. 2016).
- **Hand mixing**. The spiked sediment or slurry is mixed by using spoons/spatulas or by hand shaking the jars containing the contaminated substrate (Klosterhaus and Baker 2010; Klosterhaus et al. 2011; Liu et al. 2015). This method is rarely used as the sole mixing procedure (Norwood et al. 2013; Fathallah 2014; Bolyard et al. 2017), but most often applied as a first homogenisation step in conjunction with and followed by mechanical methods including rolling (Jeppe et al. 2017b; Mehler et al. 2017; Sinche et al. 2018). Hand mixing implies brief mixing times and is usually performed continuously during the addition of the spiking solution (Hartzell et al. 2018) and for 5–20 min after spiking, to accomplish the homogenisation (Fathallah 2014; Liu et al. 2015; Gomiero et al. 2018).

A relevant portion of the analysed papers reported undefined information concerning the mixing methods, especially in the case of artificial sediments (Fig. 6B). Beyond the unclassifiable methods, mechanical stirring, sediment rolling and mechanical shaking methods are the most used for homogenising the sediments (Fig. 6A) and especially field-collected sediments (Fig. 6B). In contrast, rotatory mixing and hand mixing (alone or in conjunction with other methods) were used less frequently.

As already observed for spiking methods, the type and environmental conditions of the substrate may be drivers for the selection of the mixing method too. For example, Ditsworth et al. (1990) proposed sediment rolling to prepare well-sorted fine sands for toxicity testing. However, substrates showing cohesiveness may need the addition of small water aliquots (Ditsworth et al. 1990; Murdoch et al. 1997) or the preparation of a slurry (Rust et al. 2004) to increase fluidity before being mixed using the sediment rolling method. Similarly, rotatory mixing is a valid method for mixing sands and incoherent substrates (Díaz-Jaramillo et al. 2016), but it does not work well for mixing cohesive sediments that tend to adhere to the vessel's wall during rotation. In general, cohesive sediments are better mixed by using mechanical stirring.

The spiking method adopted is a critical factor driving mixing times. In the overlying water spiking method, homogenisation of the substrate is not critical since the exposure to the toxicant is expected to occur through the water phase rather than through the sediment. As a consequence, mixing times are reduced to a minimum (up to 20 min). For all the other methods, homogenisation of the substrate is essential and mixing time longer: commonly over 4 h for coating methods and slurry spiking and over 24 h for dilution mixing.

Although the homogeneous distribution of the contaminant within the spiked substrate is the main purpose of mixing, only a limited number of research ($n = 37$) reported data or information concerning the evenness of chemical concentrations in the substrate. In these studies, the mixing efficiency was judged from coefficients of variation (CV) of measured sediment concentrations or deviations from the mean value (Word et al. 1987; Ditsworth et al. 1990; Call et al. 2001). Sediment rolling ($n = 12$), mechanical stirring ($n = 12$) and mechanical shaking ($n = 8$) are the mixing method for which data are available concerning mixing efficiency. The relatively low number of studies reporting mixing efficiency, together with the large number of other variables involved (substrate physicochemical features, type of solvent carrier, mixing times, etc.), makes any attempt to identify the more efficient mixing method inconclusive but allow for some comparisons.

As concern sediment rolling, in the original paper describing the method, Ditsworth et al. (1990) observed fluoranthene concentrations were not significantly different within various locations in the jar and reported a CV of 11.5%. Similar or even lower values for fluoranthene were also reported by Ciarelli et al. (1999), Driscoll and Landrum (1997) and Driscoll et al. (1997), while Stewart and Thompson (1995) observed that higher homogeneity of fluoranthene was accomplished when sediment rolling is coupled with shell coating spiking (CV = 6–12%) as compared with conventional (CV = 10–63%), sediment coating (CV = 14–45%) and sediment slurry method (CV = 15–81%). An even distribution of the contaminant within the spiked sediment was also observed for methiocarb (CV = 5.8–12.3%), lindane (CV < 20%) and acridone (CV = 6.9–15.6%) (Ciarelli et al. 1997; Péry et al. 2003; Paumen et al. 2008). In contrast, poor homogeneity was observed for phthalates (CV > 100%), hexachlorobenzene (CV = 28–62%), LAS (CV = 66%), acridine and phenanthridine (CV = 9–59% and CV = 25–60%, respectively) (Fuchsman et al. 1998; Call et al. 2001; Paumen et al. 2008; Rico-Rico et al. 2009).

Literature data concerning mechanical stirring suggest this mixing method may provide a very high mixing efficiency and distributes homogeneously the contaminants in the sediments. Coefficient of variation less than 15% and variations among replicates less than 10% were observed

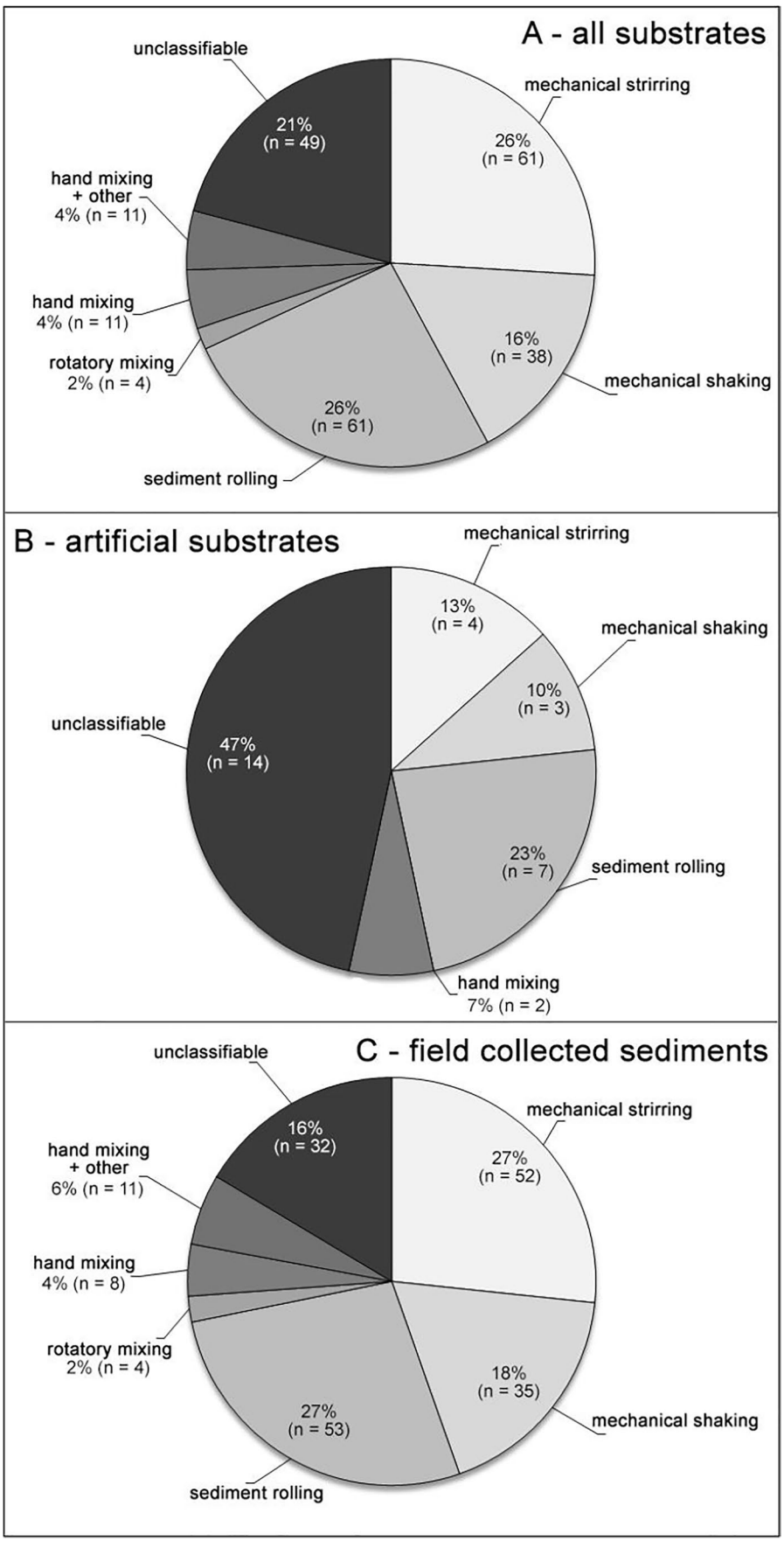


Fig. 6 Mixing methods employed for homogenising the spiked solution onto sediments. In panel **A**, data are reported by pooling the type of substrate (artificial substrate, field-collected sediment, composite and field-collected soil). Panel **B** shows methods used for mixing artificial substrates, while panel **C** reports the methods used for field-collected sediments

for chemicals such as permethrin, DDT, perfluoroalkylic substances, PAHs, PCBs and organochlorine pesticides (Oliver 1987; Landrum et al. 1992; Mulsow and Landrum 1995; Schuler and Lydy 2001; Schuler et al. 2002, 2003; Rosen and Lotufo 2005; Ding et al. 2013; Fang et al. 2016). However, also in the case of mechanical stirring, CV up to 40% were observed, indicating that the toxicant is not evenly distributed within the spiked substrate, as in the case of 4-nonylphenol, DDE, PBDE, fipronil and triclosan (Croce et al. 2005; Tian et al. 2012; Dang et al. 2016).

Mechanical shaking allowed for the preparation of well-homogenised substrates for testing with several chemicals, including PAHs, LAS, polydimethylsiloxane, chlorpyrifos and endrin (Nebeker et al. 1989; Green and Chandler 1996; Chandler et al. 1997; Henry et al. 2001; Rico-Rico et al. 2009; Vignet et al. 2014). For all these chemicals, mixing was very effective and produced CVs in the range 2.5–28.3% (Nebeker et al. 1989; Green and Chandler 1996; Rico-Rico et al. 2009; Vignet et al. 2014) or a variation among replicates less than 10% (Chandler et al. 1997; Henry et al. 2001). Poor homogeneity was obtained for radioactively labelled DDT and commercial mixtures of pyrethroids (Word et al. 1987; Van Geest et al. 2014). In particular, Word et al. (1987) observed that the use of glycine as a carrier after the coating with radioactively labelled DDT may improve significantly the performance of mechanical shaking (CV > 99% without glycine, CV = 22–24% with glycine carrier).

Equilibration

Before being used for chemical and ecotoxicological analyses, the spiked sediment has to be stored for adequate time to allow the partition of the toxicant between solid phase and interstitial water. According to the USEPA (2002), when specific equilibrium times for a given toxicant are unknown, at least 1 month of equilibration should be allowed, and 2 months or more may be necessary for chemicals with a high octanol–water partition coefficient (K_{OW}). Nevertheless, when non-persistent organic chemicals are of concern, equilibrium time may be shortened to avoid the microbial and physical degradation of the compound during ageing. However, the analysis of the literature revealed that equilibration times vary considerably irrespectively of K_{OW}, and also when a specific toxicant is of concern. As an example, equilibrium times for fluoranthene (K_{OW} = 5.2; Mackay et al. 1992) ranged from 24 h up to 60 days (Stewart and Thompson 1995; Driscoll and McElroy 1996; Driscoll and Landrum 1997); similarly, for the organochlorine pesticides DDT (K_{OW} = 6.2; Mackay et al. 1992) and dieldrin (K_{OW} = 5.5; Hansch et al. 1995), equilibrium phase lasted from a few days (Mulsow and Landrum 1995; Standley 1997; Di et al. 2017) up to 37 and 60 days, respectively for dieldrin and DDT (Hoke et al. 1995; Lotufo et al. 2001c). In general, increased equilibration periods tend to reduce the bioavailability of the organic pollutants and their toxicity towards the benthic organisms, as a consequence of an increased partition between organic carbon and porewater with the increasing contact time (Landrum et al. 1992; Xu et al. 2008; Ding et al. 2013; Hiki et al. 2021).

Study design and methodological constraints often drive the choice of the equilibrium time, while chemical analyses to verify the stabilisation of porewater concentrations before performing ecotoxicological tests are seldom performed (n = 7). As a consequence, information concerning the stability of contaminant partitioning between sediment and porewater before testing is available for a limited number of organic toxicants, including DDT and its degradation products p,p′-DDD (Word et al. 1987; Nebeker et al. 1989; Ingersoll et al. 2005), dieldrin (Nebeker et al. 1989), phthalates (Call et al. 2001) and alcohol ethoxylates (Droge et al. 2008).

Word et al. (1987) measured porewater concentrations over a period of 50 days to verify the partitioning of DDT between solid phase and water phase in the sediment and observed that a period of over 1 month is needed for achieving stabilisation. In this case, the authors assumed that equilibrium was achieved when the concentration curve of porewater concentrations reached an apparent asymptote or three consecutive measurements of DDT in porewater differed by less than 10%. Similarly, Nebeker et al. (1989) noted that after a period of 6 up to 8 weeks of equilibration, porewater DDT and endrin concentrations did not change significantly during toxicity tests with amphipods. In contrast, a 30-day equilibration time provided stable porewater concentrations only for sediment spiked with low concentrations of p,p′-DDD (3–11 μg DDD gOC^{-1}; CV < 20%), while for sediment dosed with higher concentration, the equilibrium was not reached even after 60 days of equilibration (Ingersoll et al. 2005). For phthalates and alcohol ethoxylates, times to equilibrium were less than 7 days (Call et al. 2001; Droge et al. 2008), while fluoranthene's porewater concentrations were still unstable after 40 days of equilibration (Kosian et al. 1999).

Spiked sediments and soils are typically allowed to equilibrate under static conditions, with sediment stored in the dark at room temperature or in a refrigerator at 4 °C (Dewitt et al. 1992; Lotufo et al. 2000, 2001c; Schuler et al. 2002; Ingersoll et al. 2005). More rarely, sediments are frozen (Vicquelin et al. 2011). An alternative approach relies on mixing the spiked sediments for brief periods at regular intervals during the static equilibration phase. Jeppe and co-authors in a series of studies on the pyrethroid pesticide bifenthrin proposed hand shaking and rolling daily or rolling three times a week during the equilibration phase (Jeppe et al. 2017a, b). Similarly, Greenstein et al. (2014) rolled

sediment spiked with pesticides for 2 h once per week, while Peeters et al. (2000) shook manually the sediment three times per day over a 19-day incubation, followed by a period of 7 days without shaking. Less frequently, a proper static equilibration phase after mixing is missing, and equilibrium is assumed to have been reached over a prolonged mixing phase (Schuytema et al. 1988, 1989; Nebeker et al. 1989; Suedel and Rodgers 1996). However, this latter approach may not be optimal for the partitioning of the contaminants: Kosian et al. (1999) observed a rapid decrease of fluoranthene porewater concentrations over a period of 168 h after an equilibrium phase of 40 days, and Leppänen and Kukkonen (2000) suggested this decrease may be due to the slow mixing maintained during the equilibration that may have kept the sediment disturbed. On the other hand, it cannot be excluded that the observed decrease in fluoranthene C_{free} could be an artefact due to an incomplete homogenisation of the toxicant on the spiked substrate; consequently, part of the sediment did not reach equilibrium during ageing, but during the testing phase.

Efficiency of the spiking procedure

An efficient spiking procedure should provide a spiked substrate characterised by actual concentrations matching the nominal ones; then, the spiking efficiency can be estimated through the percentage of the measured concentration compared to the nominal value, namely the percentages of recovery.

Our review retrieved information concerning the recovery from 111 research articles out of 224 selected items (49.6%). This percentage is relatively low, especially if we consider the relevance of the confirmation of the spiking concentration when a study aims to replicate an environmental concentration in the laboratory. When data on recovery are missing, or actual concentrations were not measured ($n = 80$), or nominal concentrations were not reported ($n = 33$), this impedes any deduction on the recovery.

Recovery varies largely among studies, also for the single contaminant (see Supplementary Material—Table S2), and it is tough to identify a procedure that may be considered more efficient than the others. Conventional spiking was efficient for some PAHs such as phenanthrene, fluoranthene and pyrene (Swartz et al. 1988; DeWitt et al. 1989; Ditsworth et al. 1990; Lotufo, 1997; Conrad et al. 2002; Barjhoux et al. 2014; Vignet et al. 2014), the pyrethroids cyfluthrin and deltametrin (Amweg et al. 2005) and pharmaceutical such as ibuprofen, triclosan and novobiocin (Moreira et al. 2016; Pusceddu et al. 2018), but the method provided poor recovery (< 50%) or very variable results for other PAHs such as benzo[a]pyrene (Peeters et al. 2000; Cachot et al. 2007; Vignet et al. 2014), other pyrethroids such as bifenthrin and permethrin (Amweg et al. 2005) and other pharmaceuticals and PCBs (Vicquelin et al. 2011; Nieto et al. 2017; Sinche et al. 2018). In a comparative study using fluoranthene as spiking compound and sediment rolling as mixing method, Stewart and Thompson (1995) obtained a more variable recovery for conventional spiking (54–118%) as compared with shell coating (68–72%). In general, coating methods showed a generally good recovery for most PAHs except benzo[a]anthracene and phenanthrene (Fay et al. 2000; Iburg et al. 2020). Poor recovery was also obtained with chlorpyrifos (Ankley et al. 1994), fluoxetine (Brooks et al. 2003), methiocarb (Péry et al. 2003), DDT and endrin (Nebeker et al. 1989; Schuytema et al. 1989). Dilution mixing was used with success for efficiently spiking with perfluoroalkylic substances except perfluorooctanoic acid (Fang et al. 2016; Chen et al. 2019), dioxins (Barber et al. 1998) and permethrin (Mehler et al. 2018), while it was less efficient for PAHs, including phenanthrene, benzo[a]pyrene and chrysene (Hutchinson et al. 2003; Cofalla et al. 2012; Brinkmann et al. 2013).

Whether a poor (or an excess) recovery is due to a non-optimal spiking method or mixing or to other factors is difficult to ascertain. Poor recovery may be due to compound susceptibility to microbial or chemical degradation during the equilibrium period, adsorption on glass containers and analytical constraints due to incomplete extraction from sediments (Ankley et al. 1994; Steevens et al. 2002; Péry et al. 2003; Amweg et al. 2005). Low recoveries of chlorpyrifos were observed for both conventional spiking coupled with mechanical stirring and shell coating coupled with sediment rolling and attributed to degradation via both hydrolysis and microbial metabolism (Ankley et al. 1994; Chandler and Green 2001). Adsorption on the wall of the jars used for sediment rolling was one of the causes of the low methiocarb recoveries observed by Péry et al. (2003); however, the authors reported that relevant amounts of the toxicant also remained in the water (800 mL) added to the jars to facilitate during mixing, highlighting that adding a quantity of water higher than the 50 mL suggested by Ditsworth et al. (1990) may compromise the efficiency of the spiking procedure. Adsorption on sample containers and discard with overlying water were also the main causes of the low recoveries observed for LAS spiked onto sediments using the sediment slurry method (Mauffret et al. 2010a, b). Nonetheless, other studies reported that sediment slurry is a more efficient method for dosing sediments with LAS than shell coating coupled with sediment rolling (Rico-Rico et al. 2009). Recovery in the spiked sediment depends also largely from the solvent used to extract the organic compounds from the substrate: Studies performed with different classes of contaminants spiked onto sediments using conventional and sediment slurry methods showed that different solvents or mixtures of polar and non-polar solvents provide

significantly different recovery for the single compound (Houtman et al. 2007; Creusot et al. 2016).

Conclusions

Several procedures were proposed in the literature for spiking organic chemicals onto sediments to perform ecotoxicological analyses. The lack of standardised protocols for spiking has allowed the development of procedures that differ for the type of substrate, preparation and handling procedures, the addition of spiking solutions, mixing methods to distribute the toxic on the substrate and the equilibration time allowed to pass before testing. This heterogeneity, together with the lack of studies comprising porewater analysis aiming to verify whether equilibration was achieved, makes it hard to identify a more suitable procedure than others for spiking hydrophobic chemicals onto sediments.

What can be concluded from the literature is that experimental design and aim of the studies exert a profound influence on all the sequential steps of the spiking procedure. In particular, test species, testing procedures and physicochemical properties of the organic contaminant are all primary factors addressing the selection of substrate type, sediment handling procedures, solvent carrier and mixing methods:

- Test species is most often the critical factor driving the choice of substrate type and handling procedures, especially when benthic species are of concern (i.e. sieving). The optimum range of grain size and TOC content, as well as high-quality food availability (i.e. labile organic matter derived from phytoplankton), are species-related ecological constraints favouring the choice of field-collected sediments rather than artificial substrates.
- Test species also address the selection of the mixing method. As an example, large invertebrates and fishes require a larger volume of sediment and larger aquaria than small invertebrates, restricting the choice of mixing methods to sediment rolling and rotatory mixing and excluding the use of hand mixing and several of the laboratory instruments used for shaking and mixing (i.e. vortex, rotary shakers, magnetic stirrers).
- Testing protocols identify the number of replicates and the number of individuals per replicate to be used for the experiments. The greater the number of individuals and replicates, the larger the volume of spiked sediment needed for testing, with consequent effects on the selection of mixing methods. Adjusting replicates to a minimum to save on volumes is not recommended, because adequate replication is necessary to assess the statistical validity of the experimental data and also calculate accurate including both point-estimate (LC/EC_{50} and LC/EC_{20}) and hypothesis-based (i.e. NOEC and LOEC) toxicity data.
- Test species and physicochemical properties of the toxicant are driving factors for the selection of the solvent carrier; ideally, the choice should be a trade-off between the toxicity of the solvent towards the test species and the solubility of the toxicant.
- Physicochemical properties of the toxicant affect the partitioning of the contaminant within the water and solid phase of the spiked sediment. Accordingly, they should be the primary driver for determining mixing and equilibration times needed to accomplish homogenisation of the substrate. When specific equilibrium times for a given toxicant are unknown, efforts should be focused on the identification of the minimum time required for homogenisation, before starting with a spiking experiment.

Once study objectives and experimental design (including test species, testing protocol and toxicant of concern) have been defined, then proper procedures for handling the substrate, adding the spiking solution and mixing may be decided accordingly.

Finally, recommendations from the literature review that should be adopted in a spiking experiment with organic chemicals include the following:

- The spiked sediment should be stored at 4 °C during equilibration, to minimise the possible biological degradation of the toxicants, and characterised for grain size, organic carbon content and concentrations of contaminant of potential concern;
- The volume of solvent carrier used to solubilise the organic compound should be reduced to a minimum, to minimise possible solvent-induced toxic effects, and an appropriate solvent blank should be always carried out together with tests on spiked sediment;
- Equilibration should be performed in the dark and at 4 °C to minimise degradation, and should be preferably conducted under static conditions not to disturb partitioning;
- Whether microbial degradation of the spiked compound is expected to occur, equilibration time should be commensurate with contaminant half-life in the sediment;
- During equilibration of the spiked sediment, concentrations of the organic chemical in the porewater should be periodically measured to check for equilibrium, especially when specific equilibrium times for a given toxicant are unknown or literature data are not conclusive;
- Before measuring porewater concentrations, the substrate should be thoroughly mixed for a few minutes, to allow homogenisation before analysis;
- Actual concentrations should be measured before testing, to assess spiking efficiency, and preferably in aliquots

collected at different locations within the container, to check for homogeneity of mixing.

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