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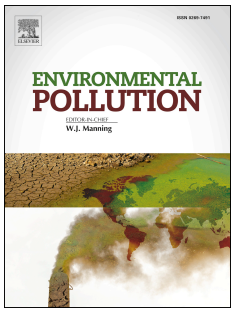

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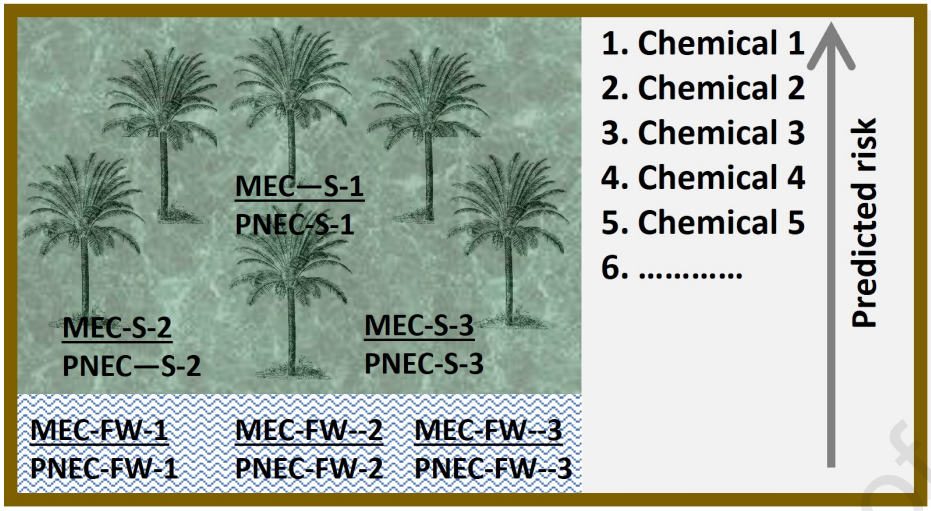

Agrochemical inputs to managed oil palm plantations are a probable risk to ecosystems: Results from a screening level risk assessment.

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Abstract

Palm oil is a high value crop widely grown in the tropics. The management of palm oil is characterised by widespread agrochemical use. Here we report the results of a screening level risk assessment conducted from the available literature on the environmental concentration of agrochemicals in surface waters and soils in palm oil growing areas. To date, only a small number of published studies have measured pollutant concentrations in and around palm oil plantations. To identify potential high-risk contaminants, a standard SSD based risk assessment, establishing risk quotients for detected contaminants, was conducted in relation to available species sensitivity distributions. A probabilistic SSD based risk assessment, calculating potential risk distributions, was also conducted for contaminants with the required number of data points available. Metals were the most commonly detected (and measured) substances and also presented the greatest risk, especially copper and zinc, but also nickel, lead and cadmium. For these metals, environmental concentrations overlapped levels found to cause effects in toxicity studies, indicating the potential for adverse outcomes from exposure. To fully understand the extent of this risk, more detailed studies are needed that assess metal speciation states and bioavailability under the prevailing soil and water chemistry conditions in palm oil plots. Limited studies have measured pesticide concentrations in palm oil systems. In these few cases, only a few active substances have been measured. From the limited information available, potential risks are indicated due to the presence of some insecticides. However, fungicides are also widely used for palm oil disease management, but little data studies are available to assess both exposure and potential effects. To further assess the potential chemical footprint of different palm oil management practices, studies are needed that systematically assess pollutant levels across a range of chemical groups to consider effects within a mixture context.

Keywords: Metals, Pesticides, Bioavailability, Species sensitivity distribution, Probabilistic risk assessment

Introduction

Palm oil is the most widely traded vegetable oil, commercially used as a biofuel, for cooking or as an ingredient in ultra-processed food, cosmetics and household products (Murphy et al., 2021). As global consumption increases, palm oil demand is likely to remain high, especially given the high productivity of oil palm systems, nine times that of other oil crops. To meet the need for palm oil, the African oil palm plant (*Elaeis guineensis Jacq*) is grown over ~19 million hectares worldwide (Murphy et al., 2021). Currently, the majority of plantations (~80%) are in Malaysia and Indonesia (FAO, 2015), although production is expanding in Thailand, Africa and South America (Vijay et al., 2016)

Oil palm is grown in relatively long lived (25-30 year) semi-permanent stands. The commercial growth of these plantations is known to have multiple environmental impacts (Myers et al., 2000; Qaim et al., 2020). The removal or disturbance of tropical forests to be replaced by palms is a major concern. Tropical forests are major sites of carbon storage, containing an estimated 37% of vegetative carbon stored worldwide (Dixon et al., 1994). Tropical forests also harbour a significant fraction of the world species (Pimm and Raven, 2000). Thus, changes in land use for oil palm production can result in the loss of high numbers of endemic species (Jantz et al., 2015), both within the planted area and outside due to habitat fragmentation (Benítez-Malvido and Martínez-Ramos, 2003; Fitzherbert et al., 2008; Leimgruber et al., 2003; Mercer et al., 2014).

While deforestation is a primary concern, the chemical management strategies used for palm oil can also impact ecosystems. Oil palm plantations are managed at a variety of scales, from large monocultures (1,000s of ha) to small holdings (1-2 ha)(Murphy et al., 2021). Chemical input is reported to be much less intensive for the small scale compared to large-scale operations, due to limited plant protection product (PPPs) and fertilizer availability; proportionately high cost; and, lack of application training for the smaller scale growers (Molenaar et al., 2013). The management strategies used for oil palm often use a combination of chemical inputs. Organic and inorganic fertilizers, empty fruit bunches and palm oil mill

effluent can all be used for nutrient input (Darras et al., 2019) }. The input of mineral fertilizer can potentially lead to soil acidification which, in turn, can negatively impact soil biodiversity (Tao et al., 2016). Further, as nutrient retention is often poor, especially in coarse lower organic matter tropical soils, these nutrients can readily leach (Tao et al., 2018) to surface waters, leading to the eutrophication and acidification of nearby lakes and rivers (Khatun et al., 2017).

In intensive oil palm management, PPPs play a significant role. Weeds are removed manually or by herbicides. This removal of the understory can exacerbate nutrient leaching (Ashton-Butt et al., 2018). One of the biggest disease threats to oil palm is basal stem rot. This fungal disease can be due to several pathogens, the most aggressive and prevalent being *Ganoderma boninense* (Rees et al., 2009). In Indonesia and Malaysia, basal stem rot infectivity of 30-45% of all palms have been recorded (Siddiqui et al., 2021), leading to 50-80% yield loss (Corley and Tinker, 2008). Although there is limited evidence to support management options (CABI, 2022; Siddiqui et al., 2021), fungicides such as thiram and hexaconazole are reportedly used prophylactically either as soil treatments, by stem painting or by injection (Mohammed et al., 2014; Turner, 1981). Insecticides and rodenticides are also applied within plantations to reduce the damage to palms and fruits from pests. In some cases, plantations deploy less chemically intensive Integrated Pest Management (IPM) strategies (Bedford, 2014; Martínez et al., 2013; Wood, 2002). However, the detection of broad-spectrum pesticides in environmental samples suggests widespread PPP use (Sharip et al., 2017a) (Elfikrie et al., 2020b).

To consolidate knowledge on the pollutants associated with palm oil, we reviewed the available literature relating to associated contaminants in production regions. From this information, we have consolidated data on (i) the environmental concentrations of contaminants present in soils and waters in, and adjacent to, oil palm systems; ii) the hazards of these chemicals for aquatic and terrestrial species; (iii) the risks of these contaminant levels evaluated through standard and probabilistic SSD based risk assessment approaches. The

results of this exposure and risk assessment can be used to identify both the potential chemicals of greatest concern in oil palm growing regions and also gaps in knowledge on the fate and risks of the agrochemicals used in palm oil plantations.

Materials and Methods

Literature Search

All literature selected for the analysis was identified following an evidence review protocol adapted from that originally published by the Collaboration for Environmental Evidence(Collaboration for Environmental Evidence, 2013). A search was conducted in all databases in Web of Science to identify publications reporting chemical application rates and/or measured concentrations of pollutant residues linked to oil palm plantations. The search terms used, and specific Web of Science databases searched, are shown in Supplementary file S1. Article titles identified from the initial search were first screened to assess if the paper was likely to contain data on either agrochemical application rates or environmental concentrations for chemicals measured in, or around, oil palm systems.

The initial candidate papers were each assessed in turn to confirm whether they contained information on agrochemical use or pollutant concentrations in palm oil areas. This could include both for locations in the plantation and those, such as surface water bodies, receiving off-site inputs through leaching and run-off. Where papers contained appropriate data, this quantitative information was extracted into two databases: one for application rates and one for measured environmental concentrations. For reports of application rates, the study information recorded related to: location, active ingredient applied, number of applications a year (if reported), and the size of the plantation. In the environmental concentrations database, the study information gathered was: location, active ingredient detected, the environmental medium measured (such as soil, surface runoff, river water etc.) and the detected concentration. Data was collected only in cases where concentrations were measured in areas where palm oil was being actively grown and managed during the time of production (i.e. any off crop control data or data collected prior to planting was not included). In cases where multiple chemicals were measured, the data for each was recorded separately.

Toxicity Assessment

Median lethal concentrations for the effects of the chemicals measured at detectable concentrations within one or more of the assessed studies were extracted from the Plant Protection DataBase, ECOTOXicology Knowledgebase and the published literature (Supplementary file 2). The available toxicity data was used to generate standard and probabilistic Species Sensitivity Distributions (SSD), from which the hazard concentration for 5% of species (HC5) for each chemical could be determine as the 5th percentile of effects on species from the fitted model (Posthuma et al., 2001; Posthuma et al., 2019). Our initial intention was to collect data to develop SSDs for effects only for tropical species (i.e., those originating from within 23°05′ north and south of the equator). However, a lack of available toxicity information for such species meant this approach was not possible. Thus, all SSDs were generated using both tropical and temperate species data. For the standard assessment, the individual SSDs were fitted for each chemical using the SSD tools package "ssdtools" in R Studio (Team, 2018). At least six toxicity data points were needed for SSD modelling. For the probabilistic assessment, a bespoke method was developed, as described below, based on the approach proposed initially by Gottschalk and Nowack (2013) and extended by Wigger et al. (2020) – the "PSSD+ method"..

Risk Characterisation

For the standard assessment, ecological risks associated with chemical residues in water samples were assessed following a standard risk assessment methodology (More et al., 2019), by taking the median and maximum measured environmental concentrations (MEC) as the exposure term and the Predicted No Effect Concentration (PNEC), derived as the HC5 value from the available SSD, as the hazard term. Risk quotients (RQs) where then calculated as $\mathrm{RQ} = \frac{\mathrm{MEC}}{\mathrm{PNEC}}$. For aquatic species, risk was estimated based on contaminants in lakes, rivers and mangroves in oil palm areas. Risks associated with exposure to contaminants was characterised based on absolute value and through the ranking of RQ values. Contaminants determined to have an RQ value >1 are predicted to pose a risk to aquatic organisms

surrounding oil palm plantations based on the data available and the assumptions inherent in the overall approach.

In addition to the standard SSD based risk assessment, for those chemicals with nine or more data points, we took a probabilistic SSD (PSSD) approach to fully represent the data and enable the generation of HC5 distributions. The approach allows for a better representation of the data and the ability to calculate risk distributions, rather than scalar RQ values. It does, however, require more data for a robust analysis. We based our method on that developed by Gottschalk and Nowack (2013) and extended by Wigger et al. (2020) – the "PSSD+ method". In short, toxicity endpoint distributions for each species were created, and each distribution sampled 10,000 times. These distribution samples were combined and plotted as a cumulative distribution to create the full PSSD curve. The HC5 of each of the 10,000 separate SSDs was obtained and used to construct an HC5 distribution. Full details can be found in the Supplementary Information and Wigger et al. (2020).

To perform the probabilistic risk assessment, lognormal probability density functions were fitted to the measured environmental concentrations and the risk estimated by assessing the similarity (and potential overlap) between this distribution and the PSSD distribution for each chemical; greater overlap indicating greater risk (Gottschalk and Nowack, 2013):

$$\mathrm{Risk}_{\mathrm{probabilistic}} = f_{\mathrm{MEC} \geq \mathrm{PNEC}_{\mathrm{min}}} \cdot f_{\mathrm{PNEC} \leq \mathrm{MEC}_{\mathrm{max}}} \quad (1)$$

where $f_{\mathrm{MEC} \geq \mathrm{PNEC}_{\mathrm{min}}}$ is the proportion of measured environmental concentration distribution that is greater than or equal to the minimum value in the PNEC distribution, and $f_{\mathrm{PNEC} \leq \mathrm{MEC}_{\mathrm{max}}}$ is the proportion of PNEC distribution that is less than or equal maximum value in the measured environmental concentration distribution. In other words, if $\mathrm{Risk}_{\mathrm{probabilistic}} = 1$ (100%), then every value in the measured environmental concentration distribution is higher than the lowest value in the PNEC distribution, and if $\mathrm{Risk}_{\mathrm{probabilistic}} = 0$, then every value in

the measured environmental concentration distribution is lower than lowest value in the PNEC distribution.

The most reported toxicological endpoints were acute LC_{50} (the median lethal concentration from acute exposure) values. As these endpoints were available for multiple species, we used LC_{50}s to build our toxicity probability distribution, but only after conversion to chronic No Observed Effect Concentrations (NOECs) by the application of an assessment factor. To do this, we divided each LC_{50} by a factor of 100. This use of this scale of assessment factors for LC_{50} values was done to align our approach with that used in the risk assessment of PPPs conducted under the current European Union (and UK) regulatory frameworks (European Comission, 2009).

For some chemicals, especially for soil pollutants, there were not enough data to allow the calculation of PSSDs for the probabilistic analysis. We placed this cut-off where there were fewer than nine toxicity endpoints and two measured concentrations. The probabilistic risk assessment was performed in Python and R, using code from Kawecki et al. (2019). Further details are provided in the Supplementary File S1, and the full methodology, code and data is archived on Zenodo (Harrison, 2023).

Results

Literature search

The initial literature search for papers that contained information on agrochemical use and resulting environmental concentrations in palm oil systems returned 2,604 hits. from which 314 titles were selected for initial screening based on the possibility that they could contain relevant data. From a further assessment of the aims and methods, 78 papers were selected for full assessment. Of these, 27 contained data that could be input into the application rate database and 24 the environmental concentration database. References for all papers from which application rate or concentration data were extracted are given in Supplementary Information S2.

Studies were reported in the literature for plantations based in Africa, Brazil, Indonesia and Malaysia. Application rate data for chemicals in oil palm plantations were extracted from all of these reported studies. Although location was not restricted in the literature search, 85% of studies containing relevant data were located in Indonesia or Malaysia. The initial set of papers were screened to collate the chemicals applied in each study. Each paper was then further screened to obtain application rates for each substance. In most studies, application rates were reported either as area measures (e.g. kg/ha, g/ha, L/ha) or for individual trees (e.g. g/palm). In some cases, application rates could not be identified for all chemicals listed. For example, some insecticides, fungicides and herbicides were identified as being used in surveys or grower interviews, with little to no further detail provided on frequency or application rates (see Table 1 for a list of applied fertilisers and pesticides and Supplementary Information S2 for all data on applied rates).

Table 1. List of substances reported to be applied as fertilisers or pesticides in oil palm plantations as identified from literature searches.

Class	Active substance
	Copper
	Metalaxyl
	Maneb

Fungicide	Captan
	Hexazinone
	Diuron
	Thiram
	Hexaconazole
Rodenticide	Chlorophacinone
	Coumatetralyl
Insecticide	Pirimiphos methyl
	Diazinon
	Chlorpyrifos
	Endosulfan
	Carbaryl
	Gamma HCH
	Cypermethrin
	Deltamethrin
Herbicide	Glyphosate
	Paraquat Dichloride
	Metsulfuron- methyl
	Fluroxypyr
	Glufosinate ammonium
	Bentazone
	Triclopyr
	Imazapyr
	MCPA (2-methyl-4-chlorophenoxyacetic acid)
	2,4-d Amine
	Imazapyr
Fertiliser	Nitrogen
	Phosphorus
	NPK Phonska
	Zinc
	Diammonium phosphate
	Calcium dihydrogen phosphate
	Potassium
	Potassium Chloride
	Phosphorus pentoxide
	Urea
	Magnesium sulphate
	Dolomite (Calcium Magnesium carbonate)

227

228 Fertiliser application rates were reported in eight studies; six in Indonesia/Borneo and one
229 each in Africa and South America. The addition of a form of nitrogen was reported in six of

these studies. Application rates range from 30-840 kg/ha/yr, although the most frequently reported values were in the 240-260 kg/ha/yr range. Levels of nitrogen addition for cereal crops in typical temperate arable situations are in the range of 200 – 300 kg/ha/yr. Thus, the most commonly reported levels of nitrogen addition in palm oil systems are consistent with or even below these values (although there are cases where rates are three times these typical broad arable crop levels). Phosphorous application rates were reported in five of the eight studies. Of the values reported for phosphorus, rates varied hugely from 5.3-840 kg/ha/yr, with values commonly in the 200-300 kg/ha/yr range. In addition, some inorganic salts (magnesium sulphate, calcium magnesium carbonate) and metals (zinc) were reported to be applied within plantations.

Only five papers described the active ingredients used as insecticides or rodenticides in oil palm. This information is shown in Table 1. From these studies, multiple rodenticides/insecticides, fungicides and herbicides were identified as being used for oil palm management in one or more studies. Two chemicals, chlorophacinone and coumatetralyl are indandione rodenticides use for pest control within stands. Substances from the organochlorine, organophosphate, carbamate and pyrethroid classes of insecticide were all mentioned as being used in oil palm in one or more studies. There was no obvious dominant insecticide used, although three organophosphates (diazinon, pirimiphos methyl, chlorpyrifos) were mentioned compared to two pyrethroid and carbamates (Table 1). The pyrethroid cypermethrin was the only insecticide listed as used in more than one study. Information on the fungicides applied in palm oil was also relatively sparse with only seven papers reporting usage. The inorganic fungicide copper was mentioned in two studies. Among the organic fungicides, hexaconazole was reportedly used in four studies compared to only once for all other reported fungicides. From the 13 papers reporting on herbicide use, the most commonly used active ingredient was Glyphosate, which was reportedly used in eight studies at application rates ranging from 400-1000 g/ha. Paraquat dichloride and glufosinate ammonium were also widely reported as being used in six and five studies respectively. All other

remaining herbicides were reported in three or less studies. The less commonly reported herbicides were from a range of classes including benzothiadiazinones (bentazone), phenylurea (diuron), pyridines (triclopry), imidazolinones (imazapyr), aryloxyphenoxypropionates (MCPA) and phenoxys (2,4-D)

Toxicity Assessment

The number and composition of the species toxicity data available will influence the shape of SSDs (Posthuma et al., 2019). The number of terrestrial and aquatic species for which toxicity data was available for each agrochemical reported as being used in oil palm are shown in Appendix 1. The availability of toxicity data varied for the chemicals assessed in this paper. The number of aquatic species for which toxicity data was available ranged from 6 to 144 depending on the chemical being tested. As such, obtaining data from species across a range of taxa was not always possible.

Risk Characterisation

A risk characterisation was conducted for the chemicals for which both exposure and toxicity data was available. Substances applied as fertilisers were not considered in this assessment, as these exert ecosystem impacts through mechanisms such as eutrophication, rather than through toxicity that can be characterised through a classical risk assessment paradigm. For the freshwater ecosystem assessment based on data from water measurements and the toxicity data available for aquatic species, the standard SSD based risk assessment based on maximum exposure concentrations identified the trace metals copper, lanthanum, zinc, nickel, aluminium, cadmium and lead as posing significant risk quotients of $RQ_{maximum}$>1. Three substance had $RQ_{maximum}$ >10, with the highest value for copper driven by a high measured concentration obtain from a neighbour lake ecosystem. Risk with an RQ>1 was also identified for the insecticide DDT. The standard assessments involving median exposure concentrations

283 identified risk (RQ_{median}>1) for DDT and the same metals as mentioned previously for
284 maximum concentrations, with the exception of cadmium and lead for which RQ_{median} was <1
285 (Table 2).

286

287 Table 2. Risk quotients as $RQ_{maximum}$ and RQ_{median} associated with reported contaminants of
288 rivers, lakes and mangroves neighbouring oil palm plantations calculated assuming a
289 predicted no effect concentration equal to the hazardous concentration for 5% of species
290 from species sensitivity distributions.

Type	Active ingredient	$RQ_{maximum}$	RQ_{median}
Trace metal	Copper	498.01	29.39
Trace metal	Lanthanum	75.76	75.76
Trace metal	Zinc	38.10	0.59
Trace metal	Nickel	24.92	3.16
Organic - Insecticide	DDT	2.43	1.24
Trace metal	Aluminium	2.41	1.15
Trace metal	Cadmium	1.94	0.032
Trace metal	Lead	1.41	0.35
Trace metal	Chromium	0.69	0.036
Trace metal	Cobalt	0.44	0.22
Organic - Fungicide	Trifloxystrobin	0.39	0.021
Organic - Insecticide	beta-Endosulfan	0.37	0.19
Organic - Insecticide	Methoxychlor	0.12	0.066
Organic - Insecticide	Chlorantraniliprole	0.10	0.072
Organic - Insecticide	Heptachlor	0.052	0.029
Organic - Fungicide	Propiconazole	0.052	0.00029
Organic - Insecticide	Aldrin	0.049	0.026
Organic - Insecticide	Endosulfan sulphate	0.049	0.026
Organic - Insecticide	alpha-Endosulfan	0.047	0.024
Organic - Insecticide	Dieldrin	0.044	0.023
Organic - Fungicide	Difenoconazole	0.043	0.0013
Organic - Fungicide	Thiram	0.030	0.015
Organic - Insecticide	Endrin	0.025	0.013
Organic - Insecticide	Imidacloprid	0.016	0.0077
Organic - Insecticide	DDE	0.014	0.0069
Organic - Insecticide	gamma-BHC	0.013	0.0069
Trace metal	Cerium	0.013	0.013

Trace metal	Arsenic	0.0047	0.0021
Organic - Insecticide	Buprofezin	0.0032	0.00013
Organic - Fungicide	Tebuconazole	0.0031	4.24 E-05
Organic - Insecticide	Chlordane	0.0029	0.0015
Trace metal	Selenium	0.0014	0.0014
Organic - Fungicide	Azoxystrobin	0.0014	0.0014
Organic - Insecticide	Pymetrozine	0.0011	0.00064
Organic - Insecticide	DDD	0.00073	0.00073
Trace metal	Strontium	0.00039	0.00039
Organic - Herbicide	Triclopyr	0.00035	0.00035
Organic - Herbicide	Fluroxypyr	3.79 E-05	2.65 E-05
Organic - Insecticide	Isoprothiolane	1.19 E-05	1.20 E-05
Organic - Fungicide	Tricyclazole	2.7 E-06	2.71 E-06
Organic - Herbicide	Glufosinate ammonium	9.97 E-07	9.97 E-07

For terrestrial below-ground ecosystems, the standard based SSD risk assessment was conducted using the available soil measurements and the toxicity data for soil species. The assessment identified the trace metals copper and zinc and the herbicide glufosinate-ammonium as posing significant risk (RQ>1) based on maximum measured concentrations and copper and glufosinate-ammonium risk with an RQ>1, based on median concentrations. Nickel had an RQ>0.3 for both maximum and median concentration indicating intermediate risk, while the risk of cadmium was low (Table 3).

Table 3. Risk quotients associated with reported contaminants of soil within and neighbouring oil palm plantations calculated assuming a predicted no effect concentration equal to the hazardous concentration for 5% of species from species sensitivity distributions.

Type	**Active Ingredient**	**RQ_{median}**	**$RQ_{maximum}$**
Trace Metal	Copper	4.73	12.10
Organic- Herbicide	Glufosinate-ammonium	1.25	2.14
Trace Metal	Zinc	0.45	1.21
Trace Metal	Nickel	0.36	0.68
Trace Metal	Cadmium	0.004	0.022

Probabilistic risk assessment

As indicated in the Methodology, for the probabilistic risk assessment, we only considered chemicals for which there were 9 or more toxicity data points for different species, and 2 or more measured concentrations. This meant we could only perform probabilistic assessments for 10 chemicals in water and 5 in soil. PSSDs were constructed for each substance. As example of which is given for imidacloprid in water in Figure 1. Supplementary Information S1 contains PSSDs for all chemicals assessed. The inset to Figure 1 shows the HC5 (PNEC) distribution extracted from the sampled SSDs. The mean of this distribution is 0.023 µg/L and the maximum predicted HC5 0.037 µg/L

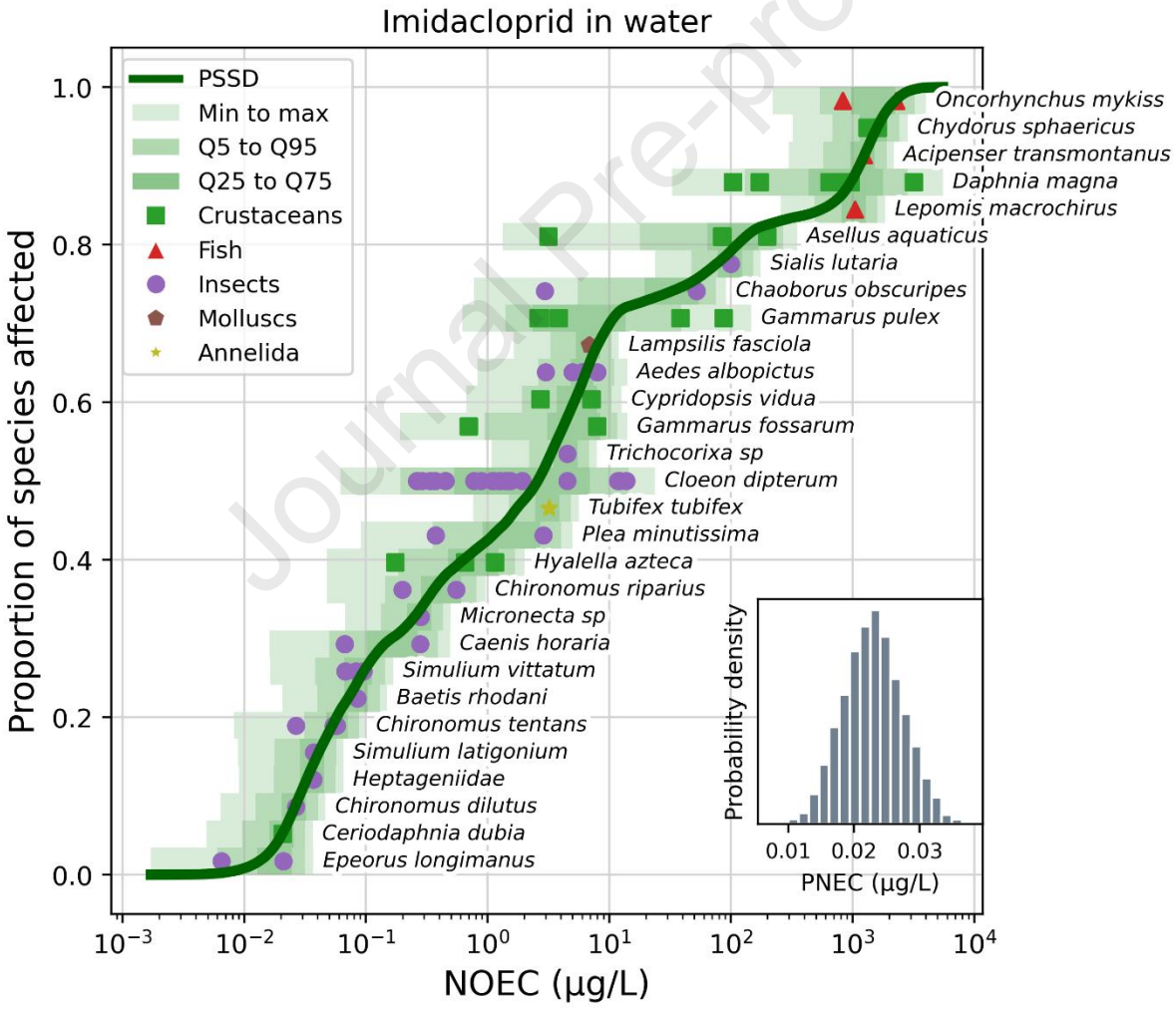
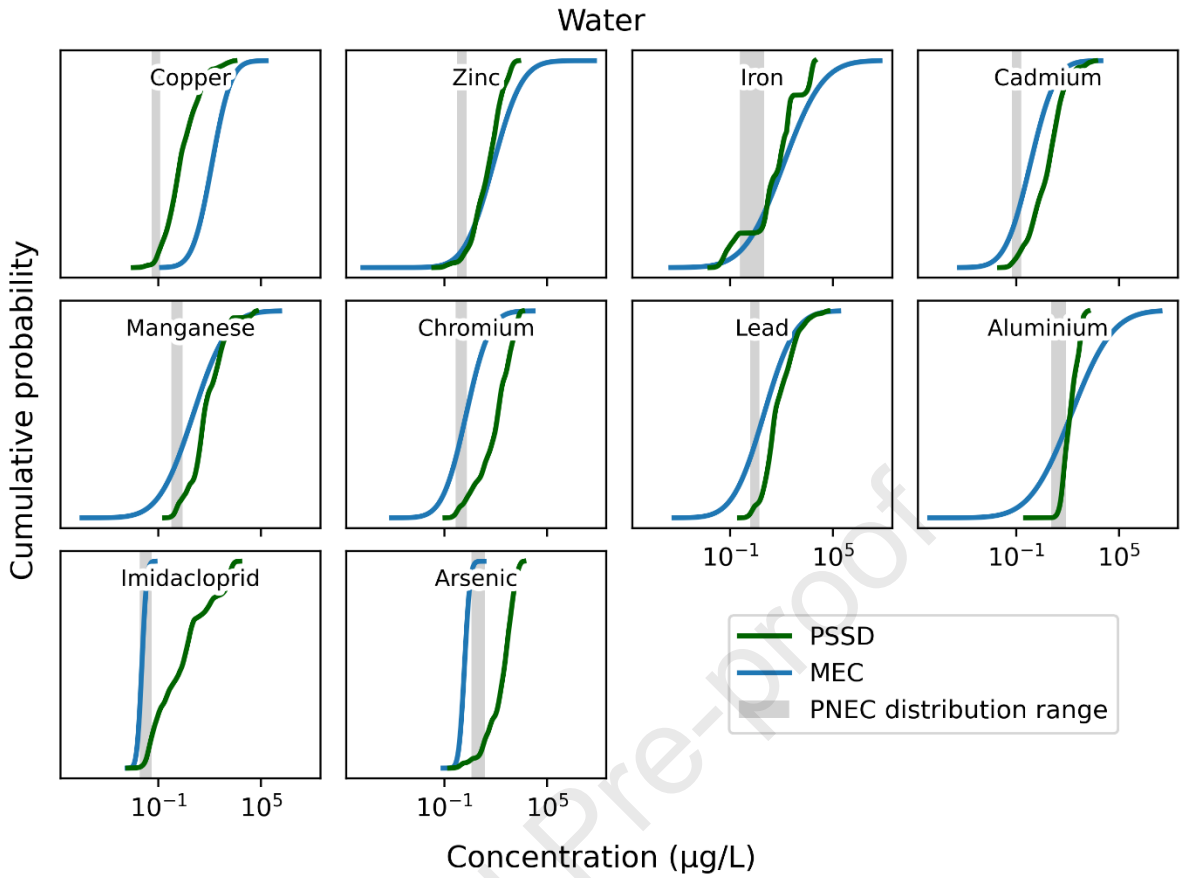


Figure 1. Probabilistic Species Sensitivity Distribution (PSSD) for imidacloprid in water. The thick green line represents the PSSD itself. The green shaded areas represent three different quantile ranges (min-max: lightest green; Q_5-Q_{95} : mid-green; Q_{25}-Q_{75} : darkest green) for each

318 species, and the markers the underlying No Observed Effect Concentration (NOEC) values
319 used for the model, which are colour- and shape-coded by taxa. The inset shows the Predicted
320 No Effect Concentration (PNEC) distribution, which is the distribution formed by taking the 5^{th}
321 percentiles from each of the 10,000 individual SSDs that form the PSSD. Note that, due to the
322 PSSD being a cumulative distribution across all species, the points in the distribution do not
323 necessarily fall in species order, and therefore the location of the species on the y-axis is
324 determined by the mean of the sampled distribution for that species.

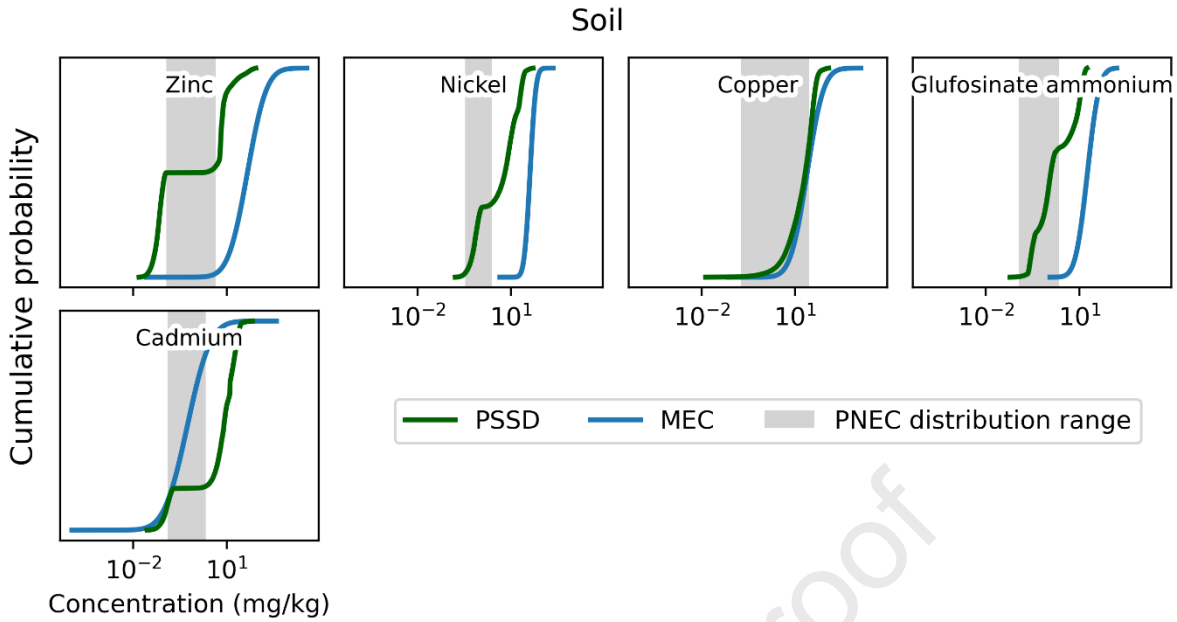
325

326 To compare the toxicity values against the exposure, we plotted the PSSDs and measured
327 environmental concentration distributions as cumulative distribution functions on the same plot
328 and visually inspected the overlap – with greater overlap indicating greater predicted risk.
329 Figure 2 shows these distribution comparisons for all compounds that could be modelled for
330 water and Figure 3 for soil. The cumulative measured environmental concentration
331 distributions can be thought of as the probability (y-axis) of finding a chemical with a
332 concentration lower than the given concentration (x-axis). For these plots, we calculated risk
333 using Equation 1 and ordered the chemicals by decreasing risk. These calculated risk values
334 are shown in Figure 4.



335

336 Figure 2. Plots of PSSDs (green) and cumulative measured environmental concentration
337 distributions (blue) in surface waters. The PNEC distribution minimum to maximum range is
338 shaded in grey. Where PSSD and measured environmental concentration distributions
339 overlap on the x-axis indicates a potential risk. The chemicals are ordered from highest to
340 lowest risk (along rows and then down columns), as calculated by Equation 1.



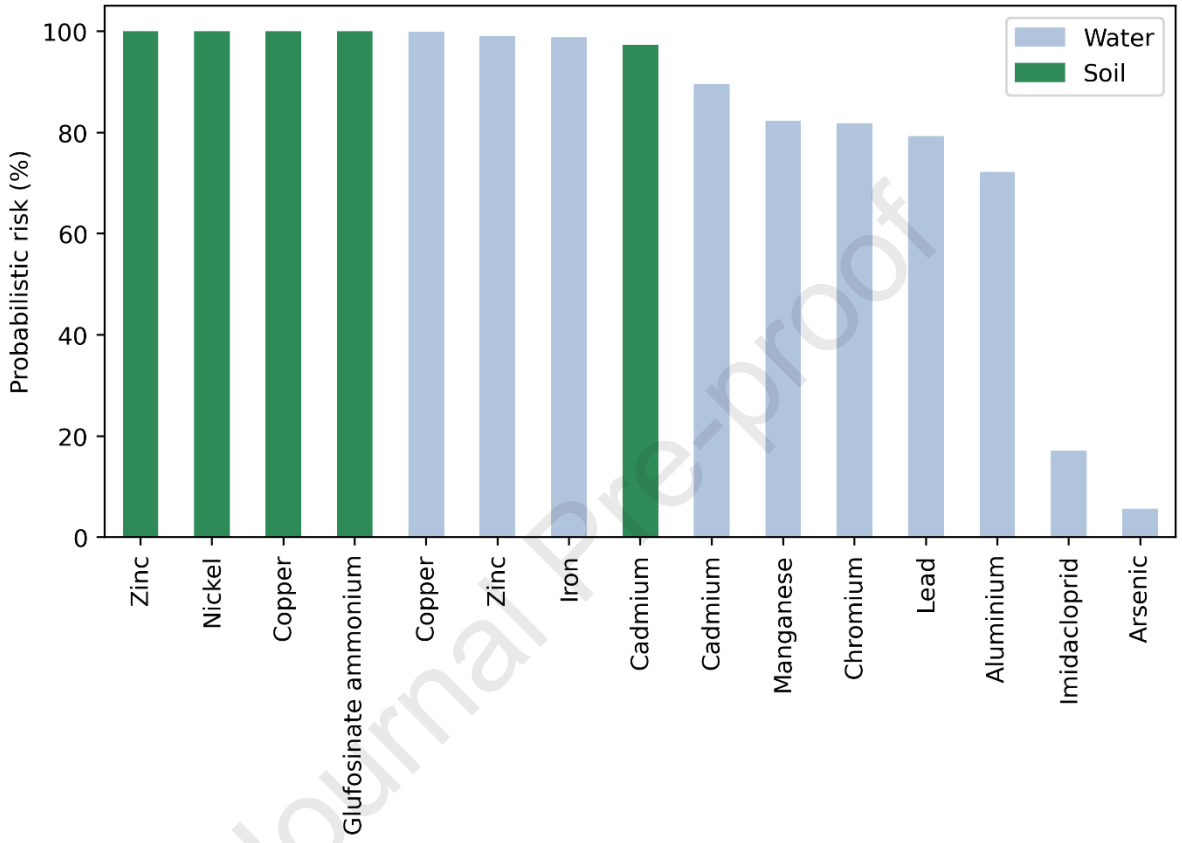
341

342 Figure 3. Plots of PSSDs (green) and cumulative measured environmental concentration
343 distributions (blue) in soils. The PNEC distribution minimum to maximum range is shaded in
344 grey. Where PSSD and measured environmental concentration distributions overlap on the x-
345 axis indicates a potential risk. The chemicals are ordered from highest to lowest risk (along
346 rows and then down columns), as calculated by Equation 1.

347

348 From the overlay of distributions, it is immediately apparent that for those chemicals with the
349 highest predicted risk, the measured environmental concentration distributions (blue lines) are
350 at notably higher values than the PSSDs (green lines). These chemicals are mainly metals,
351 for which it should be noted that no correction for bioavailability has been made in this
352 assessment, due to a lack of required soil and water chemistry data across the studies.
353 Therefore, the bioavailable fractions are likely to be lower than the measured concentrations
354 (Lofts et al., 2005). However, while our approach is conservative, even applying order-of-
355 magnitude bioavailability correction would still result in significant predicted risk for the most
356 highly ranked cases (e.g. copper, zinc, nickel in water, copper in soils). It is also notable that
357 in all cases, the measured environmental concentration distributions exceed or overlap the
358 PNEC distribution, meaning that at least at the highest concentrations likely present in the

359 environment, level of each agrochemical are higher than the highest predicted PNEC. This is
360 further reinforced in Figure 4, which highlights that no chemicals have a probabilistic risk of
361 0% (no overlap between the two distributions), and 13 of the 15 chemicals assessed have a
362 probabilistic risk of greater than 50%.



363

364 Figure 4. Risk predicted by the probabilistic risk assessment for chemicals in waters (light
365 blue) and soils (green), as calculated by Equation 1. The value for risk is 0% when measured
366 environmental concentration distributions and PSSDs do not overlap at all and 100% when
367 the distributions completely overlap. For chemicals with the same calculated probabilistic risk,
368 the distance between the mean of the measured environmental concentration distribution and
369 PSSD is used to order the chemicals.

Discussion

Oil palm is a highly productive crop that makes a significant contribution to the global vegetable oils market. In countries where it is grown, oil palm provides a significant source of income to governments and farmers from large scale producers to smallholders. As a high value crop often established by clearing tropical forest, there are commercial pressures to maximise yields. Under such requirements the use of fertilisers and other agrochemicals for agronomic management is a key component of productivity (Murphy et al., 2021).

Oil palm plantations are established across a range of soil types including tropical peats, highly weathered soils, such as acrisols, ultisols, oxisols, and developing soils, such as inceptisols and entisols. To allow production across this range of soils, management interventions, including nutrient supplementation and irrigation are crucial to productivity. The high absolute and maximum rainfall levels in tropical palm oil regions, means that the risk of fertiliser leaching, potentially leading to eutrophication, in the catchments of oil palm growing areas is high. Fertilisers, as used for oil palm, can also carry significant amounts of co-associated trace metals (Atafar et al., 2010; Li et al., 2008; Zarcinas et al., 2004). These contaminants can build up in soils and, from there, leach to surface waters. Consistent with this potential for release, the risk assessments conducted here indicated that metals were the group of contaminants presenting the highest risk in both soils and waters. For example, the distribution of measured copper water concentrations exceeded the PSSD for this metal, whilst those for zinc and iron overlapped, and those for lead and cadmium were only marginally lower. For soils, measured copper distributions also overlayed the PSSD, along with those for zinc, cadmium and nickel which were only marginally below. The exceedance of toxicity thresholds for metals indicates the potential for effects on both aquatic and terrestrial communities in oil palm systems.

The identification of metals as high-risk substances in waters is consistent with the results from previous prioritisation work. Johnson et al. (Johnson et al., 2017) conducted a chemical "risk ranking" study for UK freshwaters using the median effect concentration for *Daphnia magna* as the hazard term and a composite set of literature and monitoring data from the Forum of European Geological Surveys and English Environment Agency as the measure of exposure. Metals represented 5 of the top 10 and 12 of the top 30 ranked substances in this assessment. Copper and zinc were two of the three highest ranked substances, along with aluminium, whilst iron also ranked in the top 10, and nickel and cadmium ranked 12th and 13th. The same median value based ranking approach was also applied by Johnson et al. (2018) to two catchments in China. Again, inorganic chemicals dominated the top risk substances (10 of the top 15), with copper and zinc the two highest ranked, iron fourth (after nonylphenol) and three other metals (cadmium, nickel, chromium) in the top ten. For soil, studies have also identified a potential risk from metals from site specific to national scale, with zinc and copper (Spurgeon et al., 2008) and cadmium identified as the highest risk substances (Spijker et al., 2011; Yang et al., 2018).

The overlapping distributions of the environmental concentrations and PSSD for metals such as copper and zinc suggest the potential for these metals to have realised effects on communities in oil palm systems. There is, however, a known challenge in translating observations of metal toxicity determined in laboratory studies to impacts in the field related to differences in bioavailability, which is linked to environmental conditions and metal "aging" processes (Lofts et al., 2005; Lofts et al., 2004; Smolders et al., 2009). Observations have identified that the form of exposure to metals in laboratory systems, where they are typically added as soluble salts, will differ from the speciation states of metals in environmental exposures (Smolders et al., 2015). Further, in the environment, factors such as pH, dissolved organic matter concentration and concentrations of major cations and ions can affect metal bioavailability (Lofts et al., 2013; Ma et al., 2006; Vaananen et al., 2018). A range of geochemical models and transfer functions exist that can incorporate the role of pH, organic

matter / humic substances and cation and anion composition of water or soil on metal speciation (Brix et al., 2020; Van Regenmortel et al., 2017). The role of speciation, pH and competing ions in mediating bioavailability can further be accounted for through the use of biotic ligand modelling approaches (Mebane et al., 2020; Qiu et al., 2015; Tiberg et al., 2022). There are challenges with applying these approaches to the current dataset to conduct bioavailability assessment, as both metal speciation and biotic ligand modelling require additional water/soil chemistry parameters (e.g., pH, dissolved organic carbon, Ca, Mg, Na and K concentrations) for their parameterisation. A full set of such data is currently missing from the available data on metal levels in oil palm systems. Therefore, the collection of such integrated datasets should be a priority to assess whether the indication of a high probability and frequency of impact predicted from this study are realised under field bioavailability conditions. Nonetheless, even with order-of-magnitude reductions in available metal concentrations, significant risk would still be predicted, and the conclusions presented here would remain largely similar.

Various fungicides, herbicides and insecticides were identified as being potentially used in oil palm management. Comparatively few studies have measured the resulting environmental concentrations as part of designed fate assessment or wider environmental monitoring, with only six such studies for surface waters (Elfikrie et al., 2020a; Halimah et al., 2005; Maznah et al., 2017; Sharip et al., 2017b; Sulaiman et al., 2020; Tayeb et al., 2017) and nine for soils (Halimah et al., 2005; Maznah et al., 2018a; Maznah et al., 2015; Maznah et al., 2018b; Maznah et al., 2017; Maznah et al., 2020; Muhamad et al., 2012; San Juan et al., 2023; Sulaiman et al., 2020; Tayeb et al., 2017). Within the conducted studies, 27 different organic pesticides have been recorded at detectable levels. Insecticides constitute the largest group, represented by 14 compounds, followed by fungicides with eight and herbicides with three. Within the standard SSD analysis for the aquatic compartment, the historically used insecticide DDT shows the highest risk with an $RQ_{maximum}$ >1. A further three insecticides (endosulfan, methoxychlor and chlorantraniliprole) and one fungicide trifloxystrobin have an $RQ_{maximum}$ >0.1.

449 The results of the standard SSD based analysis are supported by the probabilistic assessment
450 for imidacloprid, predicting low risk. However, for many of the detected organic pesticides,
451 there were not enough data points to conduct a probabilistic risk assessment. In addition,
452 disparities were found between types of insecticides applied and those detected in the
453 environment. For example, the insecticide cypermethrin was reported to be applied at 6.3
454 g/ha, but was undetectable in the soils or waters sampled in the literature.

455 Differences in environmental concentration and associated risk with imidacloprid, pymetrozine
456 and cypermethrin could be linked to a range of causes related to their authorisation date,
457 usage and application routes. Cypermethrin is a more historic active ingredient than either
458 imidacloprid or pymetrozine, being introduced into widespread use in the 1970s, compared to
459 the 1990s. Therefore, cypermethrin usage may have reduced following the introduction of
460 newer active ingredients onto the market. In addition, cypermethrin is commonly used for pest
461 treatment in spray formulations. Such sprays when falling onto the leaf surfaces can potentially
462 leach to surface waters, but the relatively low water solubility may limit leaching. Conversely,
463 imidacloprid and pymetrozine are used as systemic insecticides applied as seed dressing,
464 which could limit their potential for leaching, although in areas where it is widely used,
465 exposure leading to effects in surface water have been identified at least for imidacloprid
466 (Casillas et al., 2022; Thunnissen et al., 2020; Van Dijk et al., 2013).

467 The available measurements indicate that a large range of pesticides may be used for palm
468 oil management. The relative paucity of measurements for many pesticides in oil palm
469 ecosystems means there are remaining questions about the nature and magnitude of the
470 potential risks of such use. Further, existing risk assessments for pesticides are conducted
471 using data from studies largely designed to reflect conditions in temperate ecosystems. The
472 condition of soil types, climate and the species used for toxicity testing may not be fully relevant
473 to tropical environments. For example, in oil palm grown on highly weathered acrisols, ultisols
474 andoxisols soils, greater pesticide leaching may occur due to the lower organic matter content,
475 while in tropical peats, retention by organic matter may reduce leaching. In both cases, the

organic matter and clay mineral contents of soils where oil palm is grown are outside of the ranges that have generally been considered in fate modelling studies in temperate regions such as Europe (Tiktak et al., 2004).

Climatic conditions in oil palm growing areas are a further factor that may modify the potential risks of pesticides in oil palm plantations if calculated based on available fate data more relevant to terrestrial ecosystems. Historically, degradation tests for PPP regulatory purposes have mainly been conducted at temperatures of 20°C or even lower (10°C). From these studies, there is now a large database of experimental half-lives at 20°C (e.g. http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm)(Matthies and Beulke, 2017). Given that temperature is a key factor that influences pesticide degradation, values at this ambient temperature may not be relevant for tropical areas where palm oil is grown. Extrapolating degradation half-lives (DT50) measured at a given temperature to different temperatures remains challenging, especially for high temperature tropical conditions. Modelling of the relationship between temperature and degradation half-life generally indicates a negative relationship. The European Food Safety Authority recommends the use of the classical Arrhenius equation for temperature correction of degradation rates between 0° and 30°C, with the distribution of analysed median Ea values from available studies supporting use of a median value of 65.4 kJ mol-1 (range 45.8-93.3 kJ mol-1). However, in a more recent meta-analysis of the temperature dependence of degradation, Campan et al. (2023) found that this relationship was valid only for correcting the DT50 in the 5-20^{o}C range, while for temperatures greater than 20^{o}C, as are common for tropical environments, the median Ea was lower (10.3 3 kJ mol-1). Further as well as affecting fate properties, climate variable such as temperature and soil moisture conditions can also have an effect on chemical sensitivity in different species (Holmstrup et al., 2010). Such findings suggest the need for adapted guidance for pesticide fate assessment in tropical settings.

The mismatch between the taxa and species commonly tested for effects and the conditions under which these tests are conducted introduces further uncertainty when assessing

503 pesticide risks in tropical ecosystems (Daam and Van den Brink, 2010). The organisms that
504 are most commonly used for regulatory pesticide effect testing consist mainly of species
505 originally collected from sub-tropical settings and since cultured under stable laboratory
506 conditions (often at 20^{o}C). The assumption in testing these species is that they provide a
507 representative assessment of sensitivity for key taxa in the receiving ecosystem. Because the
508 organisms used for testing are generally highly amenable to mass rearing for culturing, their
509 representativeness for field species with different habitat and climate preferences has been
510 widely questioned (Chapman et al., 1998). Thus, the use of data for standard test organisms
511 to predict risk for tropical communities could be further compromised if there is evidence of
512 systematic difference in sensitivity between temperate and tropical species. Two studies have
513 compared the comparative sensitivity of temperate and tropical organisms for a range of
514 chemicals (Kwok et al., 2007; Santos et al., 2023). In both studies, the dominant comparative
515 trend was for greater sensitivity for the temperate (including the majority of species commonly
516 used for regulatory pesticide testing) compared to tropical species. For example, Santos et al.
517 (2023) found greater temperate sensitivity in 84% of comparisons for fish, 78.1% for
518 invertebrates and 96% of plants. Within this overall trend, some cases of greater sensitivity for
519 tropical species were found, including for some pesticides such as chlorpyrifos, although
520 seemingly not across Cladoceran species (Raymundo et al., 2019). Further, concerns have
521 been raised that some taxa that play significant functional roles in tropical ecosystems are not
522 represented among the commonly detected taxa (e.g. termites as ecosystem engineers in
523 tropical terrestrial environments).

524 Exposure to pesticides under environmental conditions that differ from those under which
525 regulatory testing occurs can also affect responses. There have been extensive studies of the
526 effects of temperature on the toxicity of chemical pollutants. Many studies have looked at how
527 constant temperature affects toxicity. Most frequently, increased severity of effect with
528 increasing temperature has been identified (Heugens et al., 2001; Holmstrup et al., 2010;
529 Laskowski et al., 2010). However, this trend is inconsistent with variations in response

between stressors and species (Cedergreen et al., 2016; Hochmuth and De Schamphelaere, 2014), driven by factors related to the toxicokinetic and toxicodynamic characteristics of the chemical (Cedergreen et al., 2013; Gergs et al., 2019). Any such interpretation of the effects of individual chemicals on tropical species should, however, consider that evidence of higher temperature effects on temperate species may not necessarily translate to such effects in tropical species that may be better adapted to life at temperatures.

While the risk assessment for individual substances undertaken here can inform on the scale of potential pollutant exposure and the substances of most concern, ultimately, as for any receiving ecosystems, actual exposure of species to contaminants is most likely to be to a mixture (Kienzler et al., 2019; Spurgeon et al., 2022). Mixture toxicity approaches founded on the use of additive models, such as concentration addition and independent action, have been shown to be effective in assessing the nature and scale of mixture effects. Further, when linked to species sensitivity distributions, these models have been shown to be valuable for assessing the proportion of species that may be affected by such exposures, based on the multi-substance potentially affected fraction (msPAF) concept (DeZwart et al., 2006; Posthuma and de Zwart, 2012; Wang et al., 2021). Within the current study, it was not possible to use the msPAF approach due to the mismatch in sampling locations between the literature studies. For full mixture risk assessment, systematic studies that measure metal and pesticide exposure and link these to community structural and functional characteristics would be invaluable for fully understanding how agrochemical use in palm oil management affects terrestrial and freshwater ecosystems.

Conclusions

We conducted a structured literature review to identify the range of agrochemicals used in oil palm plantations and the concentrations of the associated substances present within and near these managed systems. Extensive fertiliser use was reported in oil palm plots in multiple studies. Generally, application rates were consistent with those for temperate arable crops,

557 although in some cases, higher inputs were reported. Multiple studies also detailed the
558 presence of trace metals in soils and waters in and around palm oil plantations, with copper,
559 zinc, cadmium, and nickel among the most commonly detected elements. The use of
560 insecticides, fungicides, and herbicides for palm oil management was also reported.
561 Insecticides and fungicides were most commonly detected in soils and water, although
562 herbicides have rarely been measured. With the indicated generalise use of plant protection
563 products in palm oil systems, especially further measurement of insecticides, fungicide and
564 herbicides in soils and freshwaters are needed to address the high degree of remaining
565 uncertainty on the range and concentrations of different pesticides present in different types
566 of palm oil system. To assess the risks of the pollutants present, standard and probabilistic
567 SSD based risk assessments were conducted. The SSD models for these assessment were
568 constructed using all available toxicity data for the relevant compound. Species data included
569 for these model were mainly from temperate species creating uncertainty whether similar
570 response would be seen in local (topical) species. A question for which further work is needed.
571 These analyses that was conducted highlighting the potential risks associated with various
572 chemicals, particularly metals, and the overlap between measured environmental
573 concentrations and predicted no effect concentrations indicating the potential ecosystem
574 effects of contaminants linked to palm oil production.

575

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581

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856

1. Metal pollutants are commonly detected in palm oil ecosystems
2. Copper, zinc, nickel, lead and cadmium may present risks in palm oil areas
3. Pesticides are widely used for palm oil management, but have rarely been measured
4. Potential risks are indicated for some insecticides.
5. Future risk assessment needs to consider bioavailability and mixtures

Declaration of interests

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

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: