Manuscript

Submitted to Environmental, Science & Technology in June 2023

https://doi.org/XXX

Legacy and Emerging Plasticizers and Stabilizers in PVC Floorings: Impacts of an Industrial Transition and Recycling

Helene Wiesinger[1*], Christophe Bleuler[2], Verena Christen[3], Philippe Favreau[2], Stefanie Hellweg[1,4], Miriam Langer[3,5], Roxane Pasquettaz[2], Andreas Schönborn[6], Zhanyun Wang[1,4,7*]

[1] Chair of Ecological Systems Design, Institute of Environmental Engineering, ETH Zürich, 8093 Zürich, Switzerland

[2] Service de l'air, du bruit et des rayonnements non ionisants (SABRA), Geneva cantonal office for the environment, 1205 Geneva, Switzerland

[3] Institute for Ecopreneurship, School of Life Sciences University of applied Sciences and Arts Northwestern Switzerland, FHNW, 4132 Muttenz

[4] National Centre of Competence in Research (NCCR) Catalysis, Institute of Environmental Engineering, ETH Zürich, 8093 Zürich, Switzerland

[5] Eawag – Swiss Federal Institute of Aquatic Science and Technology, 8600 Dübendorf

[6] Institute of Natural Resource Sciences, ZHAW Zurich University of Applied Science, 8820 Wädenswil

[7] Empa – Swiss Federal Laboratories for Materials Science and Technology, Technology and Society Laboratory, 9014 St. Gallen, Switzerland

* Contact information: Helene Wiesinger: wiesinger@ifu.baug.ethz.ch; Zhanyun Wang: zhanyun.wang@ifu.baug.ethz.ch

ABSTRACT

Hazardous chemicals in building and construction plastics can lead to significant indoor exposure, health risks, and contamination of recycled materials. We systematically sample new PVC floorings on the Swiss market (n=151). We conduct elemental analysis using XRF, targeted and suspect GC-MS analysis of *ortho*-phthalates and alternative plasticizers, and bioassay tests for cytotoxicity, oxidative stress, and endocrine, mutagenic, and genotoxic activities (for selected samples). Surprisingly, 16% of the samples contain regulated chemicals above 0.1 weight%, mainly *lead* and *bis(2-ethylhexyl) phthalate* (*DEHP*). Their presence is likely linked with the use of recycled PVC in new floorings, highlighting that uncontrolled recycling can delay the phase-out of hazardous chemicals. Furthermore, 29% of the samples contain *ortho*-phthalates besides *DEHP* (mainly *diisononyl* and *diisodecyl phthalates*, *DiNP* and *DiDP*) above 0.1 weight%, and 17% of the 85 tested samples cause certain adverse biological effects. Together, they make up an additional 35% of samples of potential concern. Moreover, both suspect screening and bioassay results indicate the presence of additional (potentially) hazardous substances, including emerging alternative plasticizers. Overall, our study highlights the urgent need for accelerating the phase-out of hazardous substances and enhancing transparency of chemical compositions in plastics to protect human and ecosystem health and enable the transition to a safe and sustainable circular economy.

SYNOPSIS

Chemicals in plastic products are currently not transparently communicated. This study highlights their importance for the ongoing industrial transition towards a safe, circular economy, using a case study of PVC flooring.

KEYWORDS

Building and Construction, Plastic additives, Chemicals of Concern, Circular Economy, Indoor Air Quality, Plasticizers, Phthalates, Recycling

1. INTRODUCTION

The building and construction sector is a major industrial user of plastics, particularly polyvinyl chloride (PVC) — in Europe 71% of PVC is used in this sector, contributing to 38% of all plastics used in the sector.[1,2] Many chemical substances are present in plastics, including residual monomers, additives, processing aids, and so-called "non-intentionally added substances" (NIASs) such as contaminants, by-products, and breakdown products.[3,4] PVC plastics have been notorious for their (earlier) extensive use of hazardous additives therein, such as *ortho*-phthalates, *cadmium*, *lead*, and *tin* as PVC requires extensive plasticization (5-65 weight%) as well as heat and UV stabilization (0.05-5 weight%).[5,6] In recent years, the use of additives in PVC are shifting, e.g., from some well-known hazardous plasticizers and stabilizers to alternative ones.[7]

Ortho-phthalate plasticizers have been associated with various adverse health effects, including lower semen quality, altered anogenital distance, endometriosis, decreased testosterone, neurodevelopmental effects, ADHD, autism, development of breast/uterine/testicular cancers, asthma, and type 2 diabetes, leading to increased regulatory scrutiny.[8,9] For example, *bis(2-ethylhexyl) phthalate* (*DEHP*, CASRN: 117-81-7) was added to the Authorisation List of the EU's Chemicals Regulation, REACH, in 2013, and a group-based regulation for all *ortho*-phthalates may be expected in the coming years.[10] Phase-out of some *ortho*-phthalates has led to an increased demand for alternative plasticizers including terephthalates, trimellitates, cyclohexane dicarboxylic acid esters, phosphates, adipates, citrates, vegetable oil derivatives, and polymeric plasticizers (see section S1 in Supporting Information (SI) 1) [7,11]. Currently, available hazard data indicate that these alternative plasticizers are likely safer than *ortho*-phthalates, but they are generally less well-studied, including a lack of important physicochemical or toxicological data for some of them.[11] Nevertheless, at least *tris(2-ethylhexyl) phosphate* (*TEHP*, CASRN: 78-42-2, likely persistent), *tricresyl phosphate* (*TCP*, CASRN: 1330-78-5, likely toxic for reproduction), and *tris(2-ethylhexyl) trimellitate* (*TEHTM*, CASRN: 3319-31-1, likely persistent and endocrine disrupting) have shown some cause for concern.[11,12]

PVC requires heat and UV stabilization, as it is intrinsically unstable due to molecular defects.[5] Earlier stabilizer systems were mainly based on *cadmium* and *lead*, which are known for posing health and environmental risks.[13,14] The PVC industry in the EU voluntarily phased out *cadmium*- or *lead*-based stabilizer systems in 2001 and 2015, respectively, and replaced them with *(organo-) tin*-, *barium*- and *calcium*-based systems.[7,15,16] Yet, some of these replacements may still lead to

diverse adverse health effects. *Organotins* are known for their endocrine-disrupting potential, ecotoxicity, neurotoxicity, and liver toxicity.[17–19] *Barium* exposure may lead to kidney diseases, neurological, cardiovascular, mental, and metabolic disorders.[20] Current regulation mainly covers legacy metal(loid) elements (*chromium*, *cadmium*, *lead*, *arsenic*, *mercury*, *nickel*), which must be below a 0.1 weight% benchmark in certain plastic products. [21–24]

Building and construction plastics contribute to long-term exposure to hazardous chemicals therein in two ways. On one hand, due to the long lifetime of these plastics, legacy chemicals that have been phased out from new production and use may still be common in products that are in use.[25–27] On the other hand, the comparatively high recycling rate of building and construction PVC plastics (17% in the EU in 2012, 16% in Switzerland in 2017) and the common practice of closed-loop recycling can prolong the presence of hazardous chemicals through contamination of new products, extending the consumer and occupational exposure to these substances.[28,29]

PVC floorings have been identified as a key source of indoor chemical exposure to hazardous chemicals, especially *ortho*-phthalates.[30–36] Despite so, only limited studies investigated the chemical compositions of PVC floorings,[37] typically with too small sample size and limited tested chemicals [36,38–43]. One study measured a large number of samples using a non-targeted screening approach; however, this study was based in the United States and may not represent the European market well, did not quantify the detected substances, and did also not screen the samples for possible biological activity.[44] Measurements of other PVC products or indoor dust, and epidemiological studies, may allow for inferences on the possible chemical content of PVC floorings, but with significant uncertainties.

In this study, we aim to comprehensively understand chemicals present in building and construction plastics, including their origins and potential impacts. Using a combination of targeted analysis and suspect screening, we determine the presence and levels of legacy and novel substances in new PVC floorings on the Swiss market, with a particular focus on plasticizers and metal(loid) heat/UV stabilizers. In addition, we test the biological activity of selected flooring extracts using several bioassays. We then contextualize our measurements and biological observations in terms of implications to human health, the environment, and the transition to a circular economy. Finally, we provide possible recommendations to researchers, policy-makers, the industry, and citizens.

2. MATERIALS AND METHODS

2.1 Overview

A total of 186 new flooring samples were collected from various do-it-yourself (DIY) stores and one flooring retailer for large-scale projects in Switzerland during 2021 and 2022. The samples were first screened using X-ray fluorescence (XRF) for their elemental compositions and Attenuated Total Reflectance – Fourier transform infrared spectroscopy (ATR-FTIR) for their polymer compositions and their *ortho*-phthalate presence. Only PVC samples (n=151), as determined by the XRF and ATR-FTIR screening, were further analyzed with GC-MS and bioassays. Subsequent analyses include using ATR–FTIR to screen the presence of *ortho*-phthalates, and then, using gas chromatography – mass spectrometry (GC-MS) to quantify the *ortho*-phthalate content and to screen for the presence of novel alternative plasticizers. A selection of samples was also tested for their biological activity using several bioassays. Detailed methods are described in the sections below.

A breakdown by sample characteristics (e.g., color, hardness, number of layers, presence of a grey layer, origin) can be found in Figure 1; more details are described on Sheet S1 in SI2. Information on the presence of recycled PVC in individual samples could not be obtained from the respective stores and retailers. Instead, the presence of a grey layer in a product may be used as a non-conclusive indicator of recycled PVC.[45]

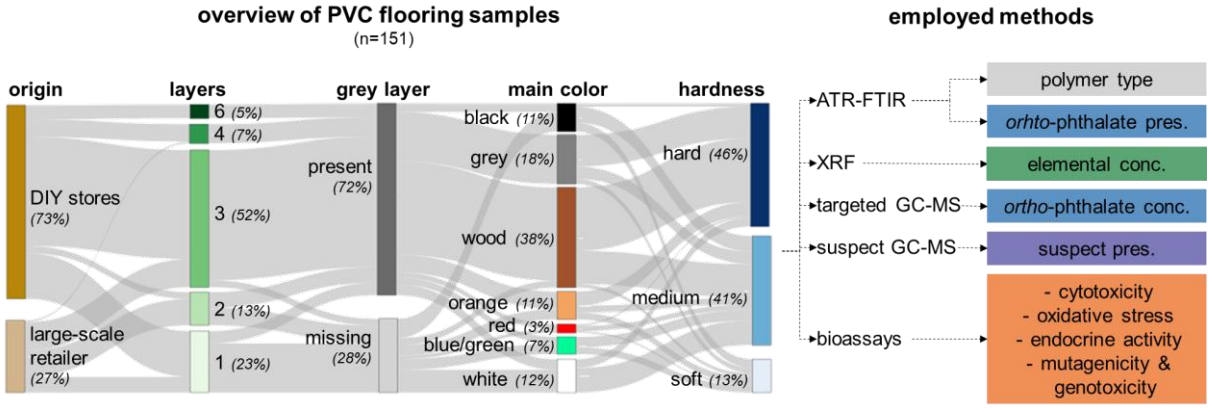

Figure 1 Schematic overview of the characteristics of the PVC samples analyzed in this study and employed methods. The presence of a grey layer may be an indication of the use of recycled PVC in the product.[45] DIY = "do-it-yourself" store; ATR–FTIR = Attenuated Total Reflectance – Fourier transform infrared spectroscopy; XRF = X-ray fluorescence; GC–MS = gas chromatography – mass spectrometry; pres. = presence; conc. = concentration

2.2Materials

An overview of the targeted and suspect compounds, their CASRNs, and further details (e.g., supplier(s)) can be found in Table S2 in SI1 and Sheet S2 in SI2 All reagents were analytical grade.

Solutions were prepared and stored in amber-colored glass vials. Reference materials with certified levels of metal(loid)s (ERM-EC681m) and *ortho*-phthalates (SPEX CRM-PVC001) were used as quality controls for XRF and GC–MS respectively (Table S3 in SI1).

2.3 Chemical analysis

2.3.1 ATR-FTIR polymer identification and *ortho*-phthalates screening

All samples (n=186) were screened with an ATR-FTIR (ThermoScientific Nicolet iS5 with iD7 ATR module) to determine the polymer type and the presence of *ortho*-phthalates (further details in section S2.3.1 in SI1, all recorded spectra in SI6-Rawdata-ATR-FTIR). Non-PVC samples (n=35) were not analyzed further.

2.3.2 XRF Screening of elemental composition

The elemental composition of all samples (n=186) was determined using a handheld XRF (Thermo Scientific Niton XL3 Gold Analyzer) with a plastic calibration (further details in section S2.3.2 in SI1, all XRF readings Sheet S3 in SI2). A certified reference material (ERM-EC681m – Polyethylene high level) was used to check operation and equipment calibration (measured values had to be within 20% of the certified levels).

2.3.3 GC-MS *ortho*-phthalate quantification

Ortho-phthalate quantification was performed on all PVC samples (n=151) using a validated method (protocol in SI3) covered in the accreditation perimeter of a laboratory complying with ISO 17025:2017. For phthalate extraction, the polymer was dissolved (in *tetrahydrofuran,* CASRN: 109-99-9), followed by matrix precipitation (in *acetonitrile*, CASRN: 75-05-8) and filtration (0.45um nylon filters, BGB SF2503-2). Subsequently, GC-MS analysis and quantification were carried out using an internal standard calibration with seventeen *ortho*-phthalates standards and seven deuterated *ortho*-phthalates as internal standards (Table S8 in SI1). All analyses were carried out on an Agilent GC-MS system (GC: Agilent 7890A, MS: Agilent 5975C) in single ion mode (SIM) with splitless injections, and compounds were separated on a DB 5MS column using a temperature gradient from 80°C to 320°C. Measurements were performed in batches, each containing calibration solutions, samples, blank solutions (procedural blank and solvent blank), and reference solutions (a solution with known concentration, and a reference material extract). From the recorded chromatograms and mass spectra (available as Agilent files in SI7-Rawdata-GCMS-Phthalates), compounds were automatically detected, identified, and

quantified using weighted (1/x) quadratic calibration curves (using the quantitative Agilent Masshunter workflow in SI4). Further details on the *ortho*-phthalate quantification workflow are in section S2.3.3 in SI1.

2.3.4 GC-MS suspect screening

All PVC samples (n=151) were screened for the presence of other suspect substances. Suspect screening in this study used a literature-adapted approach on GC-MS and focused on alternative plasticizers, antioxidants, and other substances. Standards of common alternative plasticizers and some antioxidants (Table S10 in SI1) were used as suspects and the method was adapted accordingly (extraction suitability check, GC-MS optimization for suspect identification, custom library creation, semi-quantitative calibration curves from a dilution series). The GC-MS parameters were adapted from Löschner et al, 2011 and optimized for the suspect substances.[46] The analyses were conducted on an Agilent GC-MS system (GC: Agilent 7890A, MS: Agilent 5975C) in scan mode with splitless injections. Generally, a nonpolar column (DB 5MS), a slow temperature gradient (8°C/min), a high final temperature (40°C to 300°C), a long runtime (55min), and a wide scan range (30-800amu) were chosen to ensure elution, separation, and identification of all contained compounds. Measurements were performed in one batch per dilution (40x / 1600x), containing all samples, regular blanks, and regular suspect standard solutions. Recorded chromatograms and mass spectra (available as Agilent files in SI8-Rawdata-GCMS-Suspect) were analyzed for the presence and approximate concentration of the suspect compounds, and for the presence of unknown substances using compound discovery (chromatogram integration or molecular feature), library identification (custom library and NIST14), and further manual and Python based data processing (qualitative Agilent Masshunter workflow in SI4, Python scripts in SI5). Further details on the suspect screening workflow are in section S2.3.4 in SI1.

2.4Testing of biological activities

Due to time and resource constraints, only selected samples were tested using a variety of bioassays, including cytotoxicity using MTT assays, oxidative stress using ROS assays, endocrine activity using YES/YAS assays, mutagenic activity using AMES assays, and genotoxic activity using planar-umuC. The same extraction procedure as above was used (section 2.3.3) except that samples were concentrated after filtration (using the Syncore system from Buchi to avoid losses of volatile substances) since most bioassays have a low solvent tolerance (MTT/ROS: maximally 0.1 volume%). Due to the high volatility of *tetrahydrofuran*, the sample volumes decreased during

197 the storage (–20°C) and transport (max 20°C for 2-3 days), and were filled up to 300 µl with
198 *tetrahydrofuran* before each assay.

199 ***Cytotoxicity and oxidative stress***: The highest possible test concentrations of randomly selected
200 extracts (n=85) were screened for cytotoxicity using MTT assays, and for oxidative stress using
201 ROS assays. Both assays were conducted on human liver cells (Huh7), according to Christen et al.
202 2014 (detailed conditions in section S2.4 in SI1).[47] Samples were categorized based on their cell
203 viability in the MTT assay (<30%: "highly toxic", 30-60%: "moderately toxic", 60–90%: "slightly
204 toxic", >90%: "not toxic"), and based on their MTT activity and their *ortho*-phthalate chosen for
205 further testing (details in section S2.4 in SI1).

206 ***Other endpoints (endocrine activity, mutagenicity, genotoxicity)***: Eight selected extracts were
207 screened for endocrine activity (including estrogenic, anti-estrogenic, androgenic, and anti-
208 androgenic activities) using XenoScreen YES/YAS assays from Xenometrix (Allschwil,
209 Switzerland). Nine **s**elected extracts were analyzed for potential mutagenic activity using Ames
210 MPF 98/100 from Xenometrix (Allschwil, Switzerland) with *Salmonella typhimurium* strains
211 TA98 (for detection of frameshift mutations) and TA100 (for detection of base substitution
212 mutations), following the manufacturer's protocol. Twelve selected extracts were analyzed for
213 potential direct genotoxic activity using the planar-umuC bioassay protocol of planar4 GmbH
214 (Stäfa, Switzerland). Further details can be found in section S2.4 in SI1.

215 # 3. RESULTS

216 ## 3.1 Presence and concentrations of chemicals detected in the PVC floorings

217 ### 3.1.1 Elemental compositions of the samples

218 The detection frequencies (DF) and concentration ranges of various elements in the 151 PVC
219 samples are demonstrated in Figure 2 and details are in Sheet S1 in SI2. The most commonly
220 observed elements besides *chlorine* (which is part of the PVC matrix) are *zinc* (DF: 96 %), *iron*
221 (DF: 76 %), *barium* (DF: 72 %), *titanium* (DF: 68 %), *tin* (DF: 58 %), and *vanadium* (DF: 46 %).
222 Surprisingly, also several potentially toxic metal(loids) including *chromium*, *lead*, *arsenic*, and
223 *nickel* are detected in 29 samples (DF: 19 %; range 0.001-1.562 weight%), with 6 samples
224 surpassing a common regulatory reference level of 0.1 weight% (mainly containing *lead*, Figure
225 4). None of the samples contained *cadmium* or *mercury*.

Correlations between some elements with the product color are observed. For example, *titanium* concentrations strongly correlated with white or transparent color. Also, the concentration of the toxic metal(loids) correlated positively with the presence of a grey layer (which may be one indication of using recycled PVC) and negatively with the number of layers (see section S3.5 in SI1). *Cadmium* and *lead* were important heat stabilizer systems before they were voluntarily phased out by the PVC industry in the EU (*cadmium* in 2000, *lead* in 2015). Today, heat stabilization for PVC in the EU has mainly been achieved using *zinc-calcium, zinc-tin*, and *zinc-barium* systems.[7,16] The observed elemental compositions provide supporting evidence for this industrial shift. In particular, no samples contained *cadmium* indicating its phase-out in new products, and most of the samples contained *zinc*, *tin*, and/or *barium* suggesting the wide use of novel heat-stabilization systems, while *calcium* could not be detected with the instrumentation in this study. However, it is noted that the presence of *lead* in several samples (DF: 9 %) is most likely associated with recycled PVC in products (see section S3.5 in SI1).

3.1.2 Plasticizers

The *ortho*-phthalate quantification with GC-MS showed that 55 samples (DF: 36 %) contain *ortho*-phthalates, ranging from 0.01-47 weight% (Figure 2 and Table S12 in SI1), most of which were also detected by ATR-FTIR screening (Sensitivity: 78%, Specificity: 85%, see section S2.3.1 in SI1). The most commonly observed *ortho*-phthalates are *DiNP* (DF: 24 %; 0.05-47 weight%), *DEHP* (DF: 19 %; 0.003-20 weight%), and *DiDP* (DF: 16 %; 0.05-28 weight%). They were mostly found in soft or medium-hard products (section S3.5 in SI1). *DBP*, *DiBP*, *BBP*, and *DEHP* have been added to the Authorisation List under the EU REACH, which means their use is prohibited on the EU market and new products made in the EU shall not contain more than 0.1 weight% of these substances (unless authorisation has been sought and granted). Nevertheless, 31 samples (DF: 21 %) still contain these legacy *ortho*-phthalates (mainly *DEHP*), ranging from 0.003 to 21 weight%, with 24 samples surpassing the 0.1 weight% threshold.

In addition to *ortho*-phthalates, alternative plasticizers are detected in 123 samples (DF: 81 %) using the suspect screening (Figure 2, Sheet S1 in SI2); the most frequently detected ones are *DEHT* [*Bis(2-ethylhexyl) terephthalate*; CASRN: 6422-86-2; DF: 56 %], *DEHA* [*Bis(2-ethylhexyl) adipate*, CASRN: 103-23-1; DF: 19 %], and *Octicizer* [2-Ethylhexyl diphenyl phosphate; CASRN: 1241-94-7; DF: 13 %]. Most alternative plasticizers were confirmed using corresponding analytical standards and approximately quantified (Table S13 in SI1), however, semi-

quantification results remain highly uncertain as no internal standard was used and some signals were outside the calibration range (even leading to implausible concentration estimates above 100 weight%, see Figure S9 in SI1) With these uncertainties in mind, *DINCH* [1,2-Cyclohexane dicarboxylic acid diisononyl ester; CASRN: 166412-78-8; 105 ± 76 weight%] and *DEHT* (61 ± 72 weight%) are present in the highest concentration. The overall plasticizer composition per sample can be found in Figure S9 in SI1. Alternative plasticizers are more common in hard samples with many layers (section S3.5 in SI1).

The observed plasticizer profiles in Figure 2 visualize the ongoing industrial shift from legacy *ortho*-phthalates such as *DBP*, *DiBP*, *BBP*, and *DEHP* to the increased use of other *ortho*-phthalates (mainly *DiNP* and *DiDP*) and alternative plasticizers (mainly *DEHT*, *DEHA* and *Octicizer*).[11] Interestingly, samples typically contain one major plasticizer, either *DiNP/DiDP* or an alternative plasticizer (Figure S9 in SI1), whereas *DEHP* was generally present along with other major plasticizers and was at comparatively low concentrations. This suggests the presence of *DEHP* is mainly due to recycling rather than intentional use.

3.1.3 Other substances detected in the suspect screening

In total, nearly 400 substances are identified using chromatogram integration and NIST library matching (Sheet S9 in SI2). Some more frequently detected substances include *oleamide* (DF: 21 %, CASRN: 301-02-0), *5-hexen-1-ol* (DF: 11 %, CASRN: 821-41-0), *dodecane* (DF: 11 %, CASRN: 112-40-3), *hexanamide* (DF: 10 %, CASRN: 628-02-4), and *isobutyric anhydride* (DF: 10 %, CASRN: 97-72-3), all identified through library matches. Some of these substances are or may be hazardous. For example, endocrine-disrupting *bisphenol A* (CASRN: 80-05-7) was present in two samples (confirmed using an analytical standard, DF: 1 %), PBT-candidate *UV-326* (library match, CASRN: 3896-11-5) was present in six samples (DF: 4 %) and *C8 - chlorinated paraffins* (matched by CASRN: 111-85-3 and CASRN: 73772-39-1) were present in two samples (DF: 1 %).

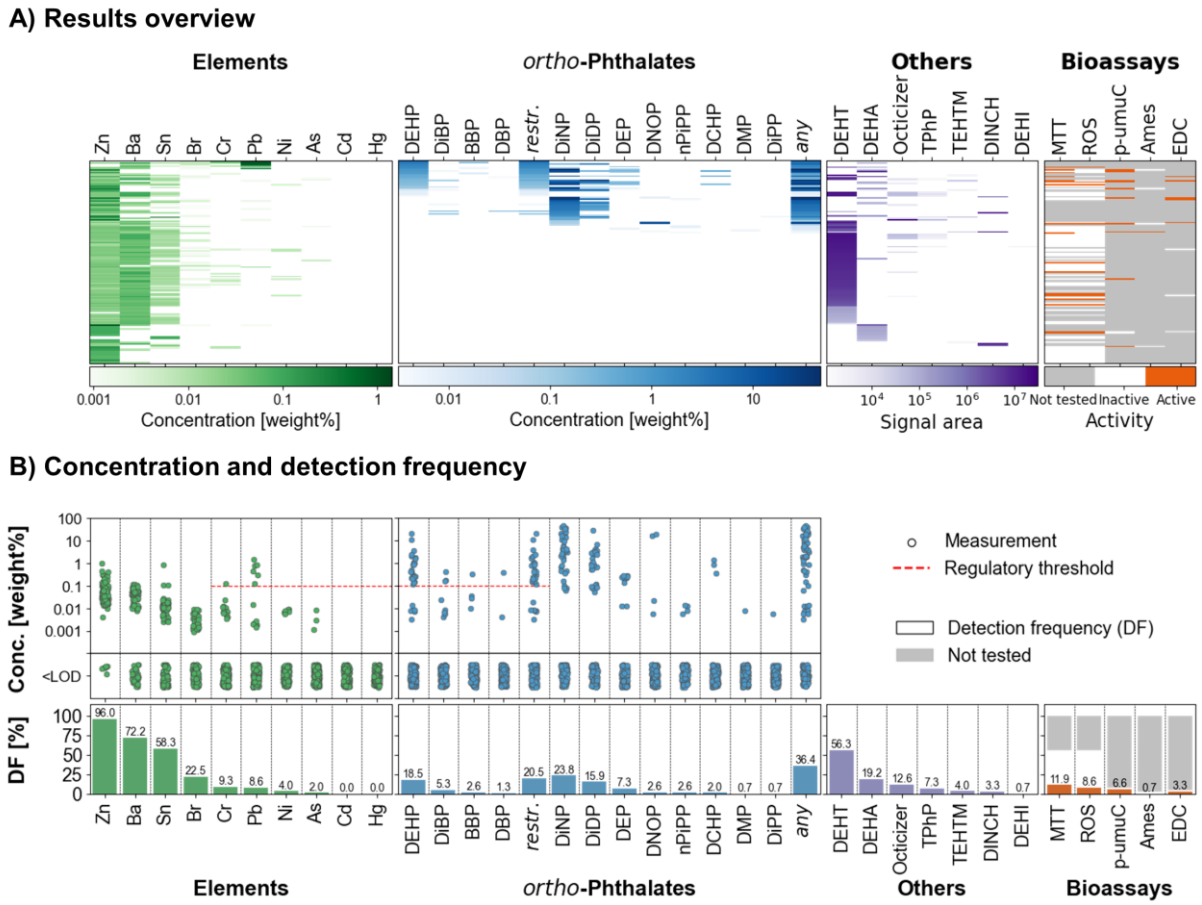

Figure 2: (A) Heatmap of concentrations of selected elements, *ortho*-phthalates, presence of alternative plasticizers, and activity in bioassay tests of 151 individual samples (every row representing one sample). (B) Measured concentrations (top) and detection frequency (DF, bottom) for selected elements, *ortho*-phthalates, alternative plasticizers, and bioassay tests. Substance acronyms can be found in Tables S12 and S13 in SI1, Conc = Concentration, DF = detection frequency, p-umuC = planar-umuC.

3.2 Bioassays

From the 85 test samples, 25 (DF: 17 %) showed some biological activities (Figure 2, Figure 3):

(1) Seven samples showed moderate cytotoxicity and clear induction of oxidative stress (ratio of oxidative stress/viability > 1.5), whereas another 11 samples displayed slight cytotoxicity. There is a clear correlation between cell viability and ROS (Figure 3).

(2) Endocrine activity was observed in five of eight tested samples and showed no correlation with cytotoxicity (Figure 3).

(3) Only one of the five tested samples showed unclear results in Ames suggesting that mutagenic potential cannot be excluded (Figure S13 in SI1).

(4) Genotoxic activity in the planar-umuC assay was observed in 11 of the 12 tested samples (Figure S14 in SI1), with one showing activity in the 1:1000 dilution, five showing activity in the 1:100 dilution, and another five showing activity in the 1:10 dilution.

Generally, these observed biological activities do not correlate with the product characteristics such as color, hardness, or presence of a grey layer, nor the content of specific chemicals detected in this study (except for endocrine activity, which only occurred in samples containing *ortho*-phthalates, see Figure 2, however, this result needs to be read with caution, as only eight samples were tested). Furthermore, while cytotoxicity and oxidative stress correlated strongly, they could not be used to predict other biological activities (Figure 3).

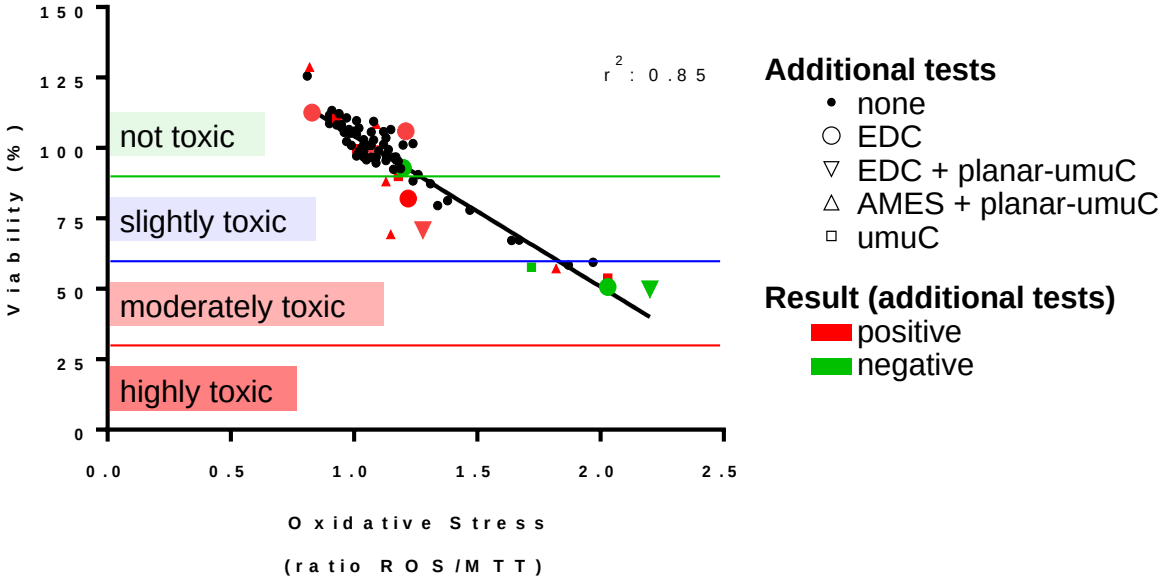

Figure 3: Biological activities of samples. Induction of cytotoxicity and oxidative stress in Huh7 cells after 24h exposure to the highest possible test concentration of the 85 PVC samples. Shown are the mean values of three independent experiments. Markers signify which bioassays were additionally tested and the marker color signifies the result of the additional tests.

4. DISCUSSION

4.1 Comparison with previous studies

Our study agrees well with previous studies on plasticizers in PVC floorings. Early studies have found *DEHP* as the major plasticizer (DF: 90 %, range: 10-18.5 weight%),[36,38–40] whereas more recent studies have reported alternative substances as main plasticizers (e.g., *DiNP*, *DINCH*, *DEHA*, *DEHI*, *TPhP*) with trace amounts of *DEHP*.[41–43,48] This industrial transition from well-

known *ortho*-phthalates to other *ortho*-phthalates or alternative plasticizers has been captured by this study. Meanwhile, it is noted that this ongoing industrial transition may have different geographical patterns. For example, the major novel and emerging plasticizers identified in this study are *DiDP*, *DiNP*, *DEHT*, and *Octicizer*, whereas a recent non-targeted screening study of PVC products in the US by Lowe et al. (2021) found distinct plasticizer profiles in flooring samples, with most samples containing *DEHA*, *DEP*, *ATBC*, *DBP*, and *BBP* (apart from *DEHP*).[44] These differences could also be due to different instrumentation and extraction procedures.

Other products made from PVC have also been studied for their plasticizer content, most studies were conducted for medical devices and toys. For medical devices, *DEHP* was commonly reported by early studies (up to 40 weight%).[49–51] In more recent studies, *DEHP* has been partially replaced with *DiNP*, *DEHT*, *DINCH*, *TEHTM*, and *ATBC*.[52–54] However, *DEHP* is still widely used in medical devices, due to it being specifically authorized for this sector within the EU (except in France).[54] In PVC toys, in addition to *DEHP* in some cases (up to 60 weight%), a transition to alternative plasticizers has been observed early on, including *DiNP* / *DiDP* (up to 40 weight%), *DINCH* (up to 25 weight%), *ATBC* (up to 25 weight%), and *TXIB* (*2,2,4-Trimethyl-1,3-pentandiol diisobutyrate*, up to 20 weight%).[55,56] A newer study of Swiss PVC toys confirmed the presence of alternative plasticizers, with *ESBO*, *DEHT*, and *TXIB* being the most common plasticizers.[57] However, *DEHP* and other legacy *ortho*-phthalates were still found in many PVC toy samples (10% in Switzerland, 30% in New Zealand, and 100% in Jordan), showing grave differences between PVC products from different regions.[57–59]. Apart from the ongoing transition, the common presence of legacy hazardous substances across a wide range of PVC products may still pose a risk of contamination to any PVC products, including flooring, should open-loop recycling take place.

To our knowledge, metals have not been studied in PVC floorings but in other PVC products. Similarly to this study, *barium* and *tin* were found to be the mainly used heat stabilizers.[60–63] Some studies have also reported *lead* and *cadmium*, which were only detected in limited to no samples in this study.[64–66] This may indicate the ongoing industrial transition to alternative heat stabilizers.

4.2 Implications of our findings on human health and the environment

Regulatory threshold comparison. A wide range of chemicals were detected in this study, with many quantified as well. Many of these substances are hazardous or potentially hazardous substances. Using a simple common regulatory threshold of 0.1 weight% (e.g., used as a threshold under the EU RoHS directive, and as a reporting threshold for substances of very high concern

(SVHC) in articles under the EU REACH), 16% of the samples show a clear cause for concern. These contain restricted *ortho*-phthalates (16%), and some additionally contain *lead* (4%) and/or *chromium* (0.5%) (Figure 4).

Meanwhile, there could be more samples of potential concern. For example, 17% of the samples (11% apart from those already identified as of clear concern above) showed activity in one of the bioassays, posing a reason for potential concern. In addition, if the 0.1 weight% threshold would also apply to other known hazardous substances (i.e. any *ortho*-phthalates, *barium*, and *tin),* 39% of samples (an additional 15% of the samples) may pose a reason for potential concern. Furthermore, if we consider that there may not be a safe threshold for the already restricted substances another 20% of the samples may pose a reason for potential concern. In total, 16% of samples show clear reason for concern and 35% of samples show potential reason for concern (Figure 4).

Furthermore, it does not mean other samples are entirely of no concern. While alternative plasticizers detected (e.g., TCP, TEHP) were comparatively safer than legacy *ortho*-phthalates, many may be present in high concentrations (especially DINCH and DEHT), and could be released continuously, and thus, act "pseudo-persistent".[11] Currently, scientific studies on the environmental and human health effects of such alternative plasticizers are ongoing, which may warrant further assessment in the future.[11,17–20] In addition, some other hazardous substances could have been present in the samples, but were not detected/quantified in this study, chemically and/or through bioassays.

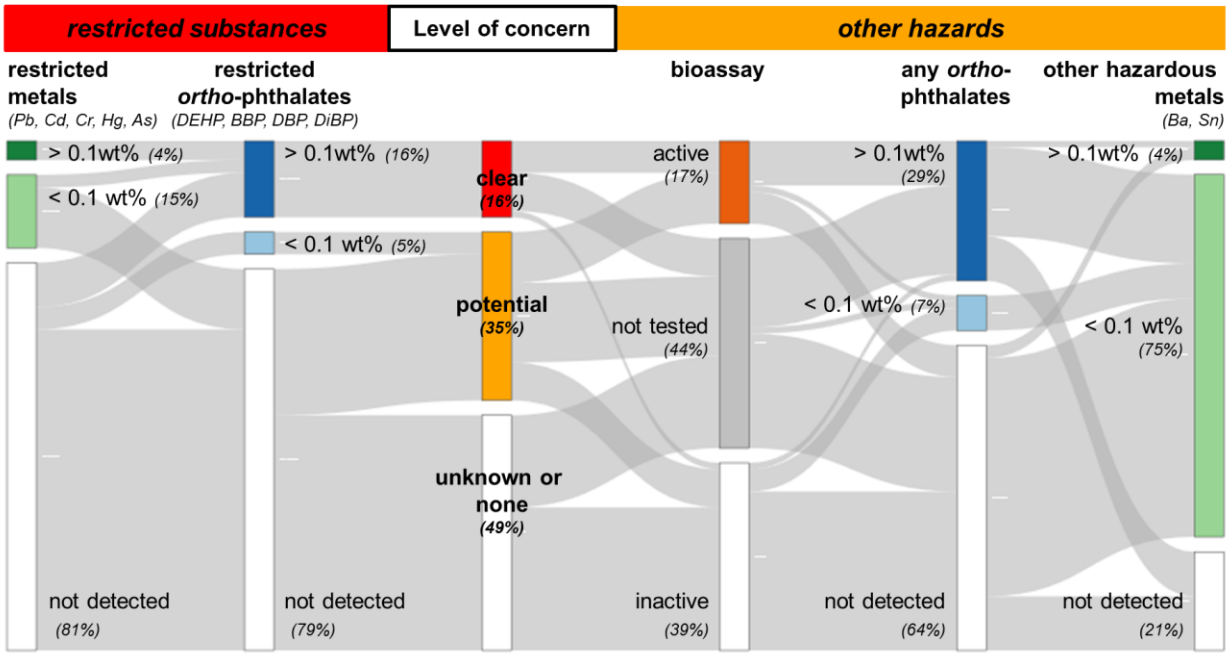

Figure 4: Samples indicating a reason for clear or potential concern. Percentage of samples containing restricted substances, mainly metal(loid)s (Pb, Cd, Cr, Hg, As) or *ortho*-phthalates, or showing activity in bioassays or containing other hazardous substances. DEHP = Di(2-ethylhexyl) phthalate (CASRN: 117-81-7); BBP = Benzyl butyl phthalate (CASRN: 85-68-7); DBP = Di-n-butyl phthalate (CASRN: 84-74-2); DiBP = Diisobutyl phthalate (CASRN: 84-69-5)

Exposure to metal(loids) and plasticizers from PVC floorings. While many substances were detected in PVC floorings, one may question whether they may be released from the products and result in actual exposure.

For metals, it is not an easy task to answer this question, as release depends on the metal(loid) form (e.g., chemical species, matrix, particle size) and several other environmental variables (e.g., environmental pH, exposure route).[67] Some previous studies have demonstrated the release and toxic effects of lead from PVC and thus show that the continued presence of toxic metals in PVC products can pose a risk to humans and the environment. [63,68]

For plasticizers, literature on exposure from PVC flooring and other sources has been abundant (see section S4.1 in SI1), with the following learnings that are relevant to our results. For *ortho*-phthalates, PVC flooring is a major contributor to indoor air and dust concentrations and is responsible for a large portion of total indoor exposure (low $\mu g\ kg_{bw}^{-1}\ d^{-1}$ range; dust, inhalation of airborne particles, and direct skin contact being the major exposure pathways).[32–36] Together with dietary intake (higher $\mu g\ kg_{bw}^{-1}\ d^{-1}$), occupational exposure, or, for some individuals, medical exposure (low $mg\ kg_{bw}^{-1}\ d^{-1}$), relevant health limit values (e.g., *DEHP reference dose*: 20 $\mu g\ kg_{bw}^{-1}\ d^{-1}$) can be approached or even exceeded.[30] Hence, the prolonged presence of (legacy)

ortho-phthalates in floorings observed in this study, may pose health risks to specific susceptible populations (e.g., toddlers).[30] This is of particular concern, as recent meta-reviews suggest that the type of health concerns posed by *ortho*-phthalates (e.g., endocrine disruption, developmental toxicity) may already occur below current "safe levels", especially when considering additive or synergistic mixture effects.[8,9,69] This suggests that many existing PVC floorings will continue contributing to *ortho*-phthalate exposure and negative human-health outcomes and that recycling of such PVC floorings may lead to further prolonging these.

For alternative plasticizers, fewer exposure assessments have been conducted.[11] Alternatives are found in similar concentrations in indoor media, albeit slightly lower than *ortho*-phthalates, and thus result in slightly lower exposures. [70–73] Currently, health limit values for alternative plasticizers (e.g., tolerable daily intake, reference dose) are either yet to be set, or orders of magnitude higher than those for *ortho*-phthalates.[11] As more research is being carried out on alternative plasticizers, this space is yet to be monitored.

Health impacts and epidemiological evidence. Exposure to plasticized PVC, be it from indoor PVC floorings or during production and recycling, has a strong link to the plasticizer concentrations in biological tissues and ultimately the occurrence of health effects in exposed populations. Several biomarkers (e.g., urine levels of metabolites, typically in the ng/mL range) were found to correlate with exposure to PVC floorings or with occupational exposure to PVC).[74–77] Several other studies point to an association of asthma and allergies with residential PVC floorings, and to the development of liver cancer in an occupational context (which is likely caused by vinyl chloride exposure, rather than additives).[78–81]

4.3 Implications of our findings on a transition to a safe, circular economy

About 16% of samples measured in this study contain legacy, regulated hazardous substances such as *DEHP* and *lead* at significant levels (Figure 4). Interestingly, these substances are often present at levels lower than typically necessary for fulfilling their functions (plasticization/DEHP: 5-65 weight%, heat stabilization/*lead:* 0.05-5 weight%), suggesting ongoing bad recycling practices (i.e., recycling of contaminated waste materials containing these substances into new products) rather than intentional use by the industry.[6] Recycling contaminated materials into long-lived products such as floorings prolongs exposure to and hampers an effective phase-out of hazardous chemicals. In fact, recycling can result in legacy hazardous chemicals remaining in products and materials for many decades after their initial use. For instance, the new PVC flooring

sampled in this study would stay relevant for waste managers until mid-2030 or later, since floorings have a long lifetime of approximately 10–15 years (this may even be increased by lifetime prolongation measures or reuse).[25] In other words, reuse, sorting, and recycling systems decades from now will still have to deal with significant amounts of hazardous substances, requiring efficient identification tools, safe disposal options, and possibly new virgin material to replace the disposed fractions. Sustainable circular economy practices have to take the chemical level into account.

However, identifying products that contain legacy or other hazardous substances is no easy task. In this study, no single product characteristics, nor analytical technique, could serve as a simple screening tool to identify all concerning samples (section S3.6 in SI1). Simple product characteristics (e.g., the presence of a grey layer, which hints at recycled content; color; hardness) were not able to identify all samples containing legacy substances or hazardous substances. For example, sorting out samples with a grey layer (66% of the samples) would remove only about 67% of the samples with legacy hazardous substances ("*Sensitivity*"), while losing a significant portion, 65%, of (comparatively) clean materials ("*100-Specificity"*). Several different screening tools are compared in section S3.6 in SI1 and Figure S15 in SI1. Also, combined approaches could not identify all concerning samples. Currently, a combination of ATR-FTIR and XRF screening is the most effective for identifying the majority of concerning samples, however, such a combination can yet not measure many other hazardous chemicals or detect mixture effects. While bioassays may be able to detect unknown substances and possible mixture effects, the bioassays employed in this study are very time- and resource-intensive. While YES/YAS assays identified *ortho*-phthalates well, time and resource constraints associated with sample extraction, preparation, and subsequent testing using these bioassays make them not suitable to realistically serve as a screening tool. Meanwhile, high-throughput screening for cytotoxicity and oxidative stress cannot be used as an indicator to replace other bioassays such as endocrine disruption, genotoxicity, and mutagenicity. Overall, the employed bioassays are time- and resource-intensive, alternative sample preparation techniques (e.g., direct sample probing, or leaching to water instead of organic solvent extraction and concentration) and higher sensitivities are required for bioassays to serve as efficient and helpful screening tools of problematic plastics.

4.4 Uncertainties and limitations of the present study

Despite utmost care and diligent quality control throughout this study, some uncertainties remain, mainly stemming from sample selection, property assignment, solvent selection, selection of analytical parameters, and selection of parameters in the data analysis.

While a large number of PVC flooring samples were collected (n=151), it is not clear how much of the PVC flooring market was captured. Some DIY stores and one retailer for large building projects were included in the selection, possibly leaving out the market of small- or medium-sized building projects (if they are considerably different from DIY and large building projects). Also, due to a lack of volume or tonnage data, the importance of individual products was unclear. Moreover, the samples in this study were all collected in Switzerland and thus may only represent this market well. While the comparison above (section 4.1) shows similarities with results from other European studies, products in other regions of the world such as North America may show quite different stabilizer and plasticizer compositions.[44]

Sample characteristics such as color, hardness, or 'containing a grey layer' were manually assigned, and thus, depend on individual perception. Due to a lack of communication on the recycling content of products in the market, the presence of a grey layer was initially used as a proxy for recycled content (as recycled PVC is often grey due to various reasons).[45,82] However, recycled materials may vary in color depending on the pre-treatment (e.g., color separation) and post-treatment (e.g., coloration), and thus, not all and not only recycled layers appear grey.

Not all substances present in PVC plastics are covered by our analyses. In other words, different extraction procedures, solvents, analytical techniques, and bioassays would need to be employed to gain complete insights into the presence of substances in the PVC products and associated biological activities.[83] For example, extraction in this study was tailored to detecting *ortho*-phthalates in PVC, while extraction of other substances that are not soluble in *THF* or *ACN*, or that are very volatile, would require other extraction techniques or solvents.[84] Similarly, the use of GC-MS is tailored for (semi-)volatile compounds, whereas for compounds that are not volatile or that degrade easily, LC-MS would be required or more suitable.[85] Furthermore, the identification of UVCBs (such as *DiDP* and *DiNCH*), for which different compositions exist on the market, and its differentiation from individual substances in the mix [e.g. *di(2-propylheptyl) phthalate* (*DPHP*, CASRN: 53306-54-0) from *DiDP*] is very difficult and not guaranteed with the standards we employed. For the bioassays, a variety of other cell lines and endpoints are available and those may have picked up on other types of toxicity.[83] Therefore, although our study is exceptionally

comprehensive in comparison to previous work in the literature, we may have missed some hazardous substances.

4.5 Recommendations for future action and research

Implementation of current regulations, including phase-out of hazardous chemicals, has generally been slow and does not sufficiently cover risks associated with chemicals in long-lived or recycled products. The presence of substances in products needs to be tracked and monitored throughout their life cycle. Initiatives such as the SCIP database in the European Union, and chemical audits by market surveillance bodies in different countries, are valuable steps in this direction, but partially require self-reporting and do not typically cover products already in use.[86,87] Importantly, more stringent and precautionary regulations would be necessary to avoid burdening future recycled materials, compromise the idea and social acceptance of a circular economy, and ensure that only clean, safe, and recyclable materials are put on the market. This may include (1) swift restriction of hazardous substances that show sufficient but not necessarily conclusive evidence for health or environmental concerns, (2) incentivize simplification and harmonization of material options, including chemical compositions, towards standard formulations, and (3) enacting extended producer responsibility toward true recyclability.[88]

Industry action has in some cases preceded regulation regarding hazardous chemicals, including the early phase-out of *lead* and *cadmium* stabilizers by the EU PVC industry. [15,16] Learning from these examples and utilizing existing industry-wide organizations (e.g. Vinyl Plus), manufacturers may pioneer and push for a swift phase-out of many more hazardous substances and transition to safer and more sustainable alternatives. Furthermore, learning from the PET water bottles, manufacturers could come together, along with other actors throughout the value chains, and establish positive lists that greatly simplify and harmonize material options and chemical composition therein toward safer and more sustainable ones.[89] The recycling industry may enhance sorting by employing already available fast screening techniques for hazardous substances at scale (e.g., using XRF for toxic metals and bromine, FTIR for *ortho*-phthalates), and thereby avoid at least some of the observed pollution of secondary materials. Nevertheless, enhancing traceability of chemicals throughout the life cycle of products is urgently needed, e.g., by labeling. This would make it possible to proactively react to current or future findings, and make informed decisions on whether and how to recycle materials or when disposal is the most sensible option. Since a digital

product passport (DPP) is currently being discussed, it would be a perfect opportunity to include the chemical compositions as well.[90]

For consumers and designers, it is difficult to judge the safety of products based on visible characteristics, neither color, presence of layers, nor did softness reliably predict the presence of hazardous substances. An independent, reliable and easily-interpretable label for building and construction products (similar to the "Blue Angel" in Germany) may simplify the decision making process for consumers. Furthermore, as citizens, more transparency, appropriate regulation, and industrial responsibility for hazardous chemicals in products can be demanded.[91,92]

Researchers should develop or improve simple, fast, and ideally comprehensive methods for identifying and removing (potentially) hazardous chemicals in plastics. Ideally, this would include screening tools that are compatible with current and future sorting infrastructure, are tolerant to contamination, and may probe the polymer directly requiring minimal pre-processing. Importantly, novel processes of removing hazardous chemicals will need to ensure high-quality output materials and lower environmental burden compared to incineration and other final disposal options.[93,94] Furthermore, researchers should fill knowledge gaps regarding hazards of commonly detected novel and emerging substances, including popular alternatives (e.g., DEHT, DiNCH, tin-zinc stabilizer), and their mixture toxicity in realistic exposure scenarios, taking into account everyday exposure from other sources as well.[95]

6. ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of the Swiss Federal Office for the Environment (8T20/17.0103.PJ), the Swiss Federal Office of Public Health (18.000809), the Canton of Zurich's Office for Waste, Water, Energy and Air (85P-1454), and the Service de l'air, du bruit et des rayonnements non ionisants (SABRA) Geneva. We thank the Cantonal Lab of Zurich for providing the XRF instrument used in this study. The human hepatoma cell line Huh7 for the MTT and ROS assays was kindly provided by Markus Heim, University Hospital Basel, Switzerland. We also thank Flavia Meyer, Caroline Buff, Armin Siegrist, Ana Agustin Navarro, and Niels Plinke for their experimental support in this project. We further thank Magdalena Klotz (ETH Zurich), Christopher Oberschelp (ETH Zurich), and Melanie Haupt (realcycle), as well as Advisory Board members of the "Clean Cycle" project for their feedback and support. Zhanyun Wang gratefully

acknowledges funding by the European Union under the Horizon 2020 Research and Innovation Programme (Project: ZeroPM, Grant Agreement Number 101036756). Zhanyun Wang and Stefanie Hellweg contributed to this publication as part of NCCR Catalysis (grant number 180544), a National Centre of Competence in Research funded by the Swiss National Science Foundation.

7. REFERENCES

1. Schwarz, A. E. *et al.* Plastic recycling in a circular economy; determining environmental performance through an LCA matrix model approach. *Waste Manag.* **121**, 331–342 (2021).

2. PlasticsEurope. *Plastics – the Facts 2022*. (2022).

3. Wiesinger, H., Wang, Z. & Hellweg, S. Deep Dive into Plastic Monomers, Additives, and Processing Aids. *Environ. Sci. Technol.* acs.est.1c00976 (2021). doi:10.1021/acs.est.1c00976

4. Geueke, B. *Dossier - Non-intentionally added substances (NIAS). Food Packaging Forum* (2013).

5. Fischer, I., Schmitt, W. F., Porth, H.-C., Allsopp, M. W. & Vianello, G. Poly(Vinyl Chloride). in *Ullmann's Encyclopedia of Industrial Chemistry* 1–30 (Wiley-VCH Verlag GmbH & Co. KGaA, 2014). doi:10.1002/14356007.a21_717.pub2

6. Wypych, G. PVC Additives. *PVC Formul.* (2020). doi:10.1016/b978-1-927885-63-5.50006-9

7. Everard, M. 5 - PVC and Sustainability. in *PVC Additives* (ed. Schiller, M.) 369–410 (Hanser, 2015). doi:https://doi.org/10.3139/9781569905449.005

8. Meeker, J. D., Sathyanarayana, S. & Swan, S. H. Phthalates and other additives in plastics: human exposure and associated health outcomes. *Philos. Trans. R. Soc. B Biol. Sci.* **364**, 2097–2113 (2009).

9. Eales, J. *et al.* Human health impacts of exposure to phthalate plasticizers: An overview of reviews. *Environ. Int.* **158**, 106903 (2022).

10. European Chemicals Agency (ECHA). Phthalates. (2023). Available at: https://echa.europa.eu/hot-topics/phthalates.

11. Bui, T. T. *et al.* Human exposure, hazard and risk of alternative plasticizers to phthalate esters. *Sci. Total Environ.* **541**, 451–467 (2016).

12. European Chemicals Agency (ECHA). *Tris(2-ethylhexyl) benzene-1,2,4-tricarboxylate (TEHTM)*. (2023).

13. World Health Organization (WHO). Exposure to lead: a major public health concern, 2nd

edition. *Preventing Disease Through Healthy Environments* (2021).

14. World Health Organization (WHO). Exposure to cadmium: a major public health concern. *Preventing Disease Through Healthy Environments* (2019).

15. vinylPlus. *The European PVC industry's experience in replacing lead and cadmium-based stabilisers*. (2014).

16. ESPA (European Stabilisers Producers Association). *Stabilisers – What ' s new ?* (2017).

17. Fent, K. *Ecotoxicology of organotin compounds*. *Critical Reviews in Toxicology* **26**, (1996).

18. Graceli, J. B. *et al.* Organotins: A review of their reproductive toxicity, biochemistry, and environmental fate. *Reprod. Toxicol.* **36**, 40–52 (2013).

19. Kimbrough, R. D. Toxicity and health effects of selected organotin compounds: A review. *Environ. Health Perspect.* **vol.14**, 51–56 (1976).

20. Peana, M. *et al.* Environmental barium: potential exposure and health-hazards. *Arch. Toxicol.* **95**, 2605–2612 (2021).

21. Naz, M., Ghani, M. I., Sarraf, M., Liu, M. & Fan, X. Ecotoxicity of nickel and its possible remediation. *Phytoremediation Biotechnol. Strateg. Promot. Invigorating Environs* 297–322 (2022). doi:10.1016/B978-0-323-89874-4.00022-4

22. Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K. & Sutton, D. J. Heavy Metal Toxicity and the Environment BT - Molecular, Clinical and Environmental Toxicology: Volume 3: Environmental Toxicology. in (ed. Luch, A.) 133–164 (Springer Basel, 2012). doi:10.1007/978-3-7643-8340-4_6

23. European Parliament & Council of the European Union. *Council Directive 2009/48/EC on the safety of toys*. *Official Journal of the European Union* **L48**, (European Parliament, 2009).

24. European Parliament & Council of the European Union. *Council Directive 2011/65/EU on the restriction of the use of certain hazardous substances (RoHS) in electrical and electronic equipment (EEE). Official Journal of the European Union* **L174**, (European Parliament, 2011).

25. Geyer, R., Jambeck, J. R. & Law, K. L. Production, use, and fate of all plastics ever made. *Sci. Adv.* **3**, 19–24 (2017).

601 26. Kral, U., Kellner, K. & Brunner, P. H. Sustainable resource use requires 'clean cycles' and
602 safe 'final sinks'. *Sci. Total Environ.* **461**–**462**, 819–822 (2013).

603 27. Wagner, S. & Schlummer, M. Legacy additives in a circular economy of plastics: Current
604 dilemma, policy analysis, and emerging countermeasures. *Resour. Conserv. Recycl.* **158**,
605 104800 (2020).

606 28. Klotz, M. & Haupt, M. A high-resolution dataset on the plastic material flows in
607 Switzerland. *Data Br.* **41**, 108001 (2022).

608 29. Ciacci, L., Passarini, F. & Vassura, I. The European PVC cycle: In-use stock and flows.
609 *Resour. Conserv. Recycl.* **123**, 108–116 (2017).

610 30. Giovanoulis, G. *et al.* Multi-pathway human exposure assessment of phthalate esters and
611 DINCH. *Environ. Int.* **112**, 115–126 (2018).

612 31. Wang, W. *et al.* Size fraction effect on phthalate esters accumulation, bioaccessibility and
613 in vitro cytotoxicity of indoor/outdoor dust, and risk assessment of human exposure. *J.*
614 *Hazard. Mater.* **261**, 753–762 (2013).

615 32. Kim, H.-H. *et al.* Health Risks Assessment in Children for Phthalate Exposure Associated
616 with Childcare Facilities and Indoor Playgrounds. *Environ. Health Toxicol.* **26**, e2011008
617 (2011).

618 33. Xu, Y., Cohen Hubal, E. A. & Little, J. C. Predicting residential exposure to phthalate
619 plasticizer emitted from vinyl flooring: Sensitivity, uncertainty, and implications for
620 biomonitoring. *Environ. Health Perspect.* **118**, 253–258 (2010).

621 34. Little, J. C., Weschler, C. J., Nazaroff, W. W., Liu, Z. & Cohen Hubal, E. A. Rapid methods
622 to estimate potential exposure to semivolatile organic compounds in the indoor environment.
623 *Environ. Sci. Technol.* **46**, 11171–11178 (2012).

624 35. Eichler, C. M. A. *et al.* Assessing Human Exposure to SVOCs in Materials, Products, and
625 Articles: A Modular Mechanistic Framework. *Environ. Sci. Technol.* **55**, 25–43 (2021).

626 36. Clausen, P. A., Hansen, V., Gunnarsen, L., Afshari, A. & Wolkoff, P. Emission of Di-2-
627 ethylhexyl Phithalate from PVC Flooring into Air and Uptake in Dust: Emission and
628 Sorption Experiments in FLEC and CLIMPAQ. *Environ. Sci. Technol.* **38**, 2531–2537
629 (2004).

37. Wiesinger, H. *et al.* Chemicals in plastics products – a literature review. *Environ. Sci. Technol.* **under revi**, (2023).

38. Afshari, A., Gunnarsen, L., Clausen, P. A. & Hansen, V. Emission of phthalates from PVC and other materials. *Indoor Air* **14**, 120–128 (2004).

39. Xu, Y. *et al.* Measuring and predicting the emission rate of phthalate plasticizer from vinyl flooring in a specially-designed chamber. *Environ. Sci. Technol.* **46**, 12534–12541 (2012).

40. Chino, S., Kato, S., Seo, J. & Ataka, Y. Study on emission of decomposed chemicals of esters contained in PVC flooring and adhesive. *Build. Environ.* **44**, 1337–1342 (2009).

41. Bohlin-Nizzetto, P. *Content and migration of chemical additives from plastic products. (NILU report 9/2022).* (2021).

42. Kumari, K. *et al.* Investigation of polybrominated diphenyl ethers in old consumer products in India. *Environ. Monit. Assess.* **186**, 3001–3009 (2014).

43. Liang, Y. & Xu, Y. Emission of phthalates and phthalate alternatives from vinyl flooring and crib mattress covers: The influence of temperature. *Proc. Air Waste Manag. Assoc. Annu. Conf. Exhib. AWMA* **2**, 1182–1198 (2015).

44. Lowe, C. N. *et al.* Chemical Characterization of Recycled Consumer Products Using Suspect Screening Analysis. *Environ. Sci. Technol.* **55**, 11375–11387 (2021).

45. Plinke, E., Wenk, N., Gunter, W., Castiglione, D. & Plamark, M. *Mechanical recycling of PVC wastes*. (2000).

46. Löschner, D. *et al.* Experience with the application of the draft European Standard prEN 15768 to the identification of leachable organic substances from materials in contact with drinking water by GC-MS. *Anal. Methods* **3**, 2547 (2011).

47. Christen, V., Camenzind, M. & Fent, K. Silica nanoparticles induce endoplasmic reticulum stress response, oxidative stress and activate the mitogen-activated protein kinase (MAPK) signaling pathway. *Toxicol. Reports* **1**, 1143–1151 (2014).

48. Shi, S., Cao, J., Zhang, Y. & Zhao, B. Emissions of Phthalates from Indoor Flat Materials in Chinese Residences. *Environ. Sci. Technol.* **52**, 13166–13173 (2018).

49. Wang, Q. & Storm, B. K. Separation and analysis of low molecular weight plasticizers in

poly(vinyl chloride) tubes. *Polym. Test.* **24**, 290–300 (2005).

50. Welle, F., Wolz, G. & Franz, R. Migration of plasticizers from PVC tubes into enteral feeding solutions. *Pharma Int.* **3**, 5 (2005).

51. Wahl, H. G., Hoffmann, A., Häring, H. U. & Liebich, H. M. Identification of plasticizers in medical products by a combined direct thermodesorption-cooled injection system and gas chromatography-mass spectrometry. *J. Chromatogr. A* **847**, 1–7 (1999).

52. Jeon, S. H. *et al.* Development and Validation of Gas Chromatography-Triple Quadrupole Mass Spectrometric Method for Quantitative Determination of Regulated Plasticizers in Medical Infusion Sets. *J. Anal. Methods Chem.* **2018**, (2018).

53. Radaniel, T. *et al.* Quantification of five plasticizers used in PVC tubing through high performance liquid chromatographic-UV detection. *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.* **965**, 158–163 (2014).

54. Den Braver-Sewradj, S. P., Piersma, A. & Hessel, E. V. S. An update on the hazard of and exposure to diethyl hexyl phthalate (DEHP) alternatives used in medical devices. *Crit. Rev. Toxicol.* **50**, 650–672 (2020).

55. United States Consumer Product Safety Comission (US CPSC). *Phthalates and Phthalate Substitutes in Children's Toys*. (2010).

56. Rastogi, S. C. Gas chromatographic analysis of phthalate esters in plastic toys. *Chromatographia* **47**, 724–726 (1998).

57. McCombie, G., Biedermann, S., Suter, G. & Biedermann, M. Survey on plasticizers currently found in PVC toys on the Swiss market: Banned phthalates are only a minor concern. *J. Environ. Sci. Heal. - Part A Toxic/Hazardous Subst. Environ. Eng.* **52**, 491–496 (2017).

58. Ashworth, M. J., Chappell, A., Ashmore, E. & Fowles, J. Analysis and assessment of exposure to selected phthalates found in children's toys in christchurch, New Zealand. *Int. J. Environ. Res. Public Health* **15**, (2018).

59. Al-Natsheh, M., Alawi, M., Fayyad, M. & Tarawneh, I. Simultaneous GC-MS determination of eight phthalates in total and migrated portions of plasticized polymeric toys and childcare articles. *J. Chromatogr. B Anal. Technol. Biomed. Life Sci.* **985**, 103–109 (2015).

687 60. Turner, A. & Filella, M. Polyvinyl chloride in consumer and environmental plastics, with a
688 particular focus on metal-based additives. *Environ. Sci. Process. Impacts* **23**, 1376–1384
689 (2021).

690 61. Ismail, S. N. S. *et al.* Heavy metals content in low-priced toys. *ARPN J. Eng. Appl. Sci.* **12**,
691 1499–1509 (2017).

692 62. Kumar, A. & Pastore, P. Lead and cadmium in soft plastic toys. *Curr. Sci.* **93**, 818–822
693 (2007).

694 63. Njati, S. Y. & Maguta, M. M. Lead-based paints and children's PVC toys are potential
695 sources of domestic lead poisoning – A review. *Environ. Pollut.* **249**, 1091–1105 (2019).

696 64. Turner, A. & Filella, M. Polyvinyl chloride in consumer and environmental plastics, with a
697 particular focus on metal-based additives. *Environ. Sci. Process. Impacts* **23**, 1376–1384
698 (2021).

699 65. Meng, J. *et al.* Effects of chemical and natural ageing on the release of potentially toxic
700 metal additives in commercial PVC microplastics. *Chemosphere* **283**, 131274 (2021).

701 66. Oyeyiola, A. O., Akinyemi, M. I., Chiedu, I. E., Fatunsin, O. T. & Olayinka, K. O. Statistical
702 analyses and risk assessment of potentially toxic metals (PTMS) in children's toys. *J. Taibah*
703 *Univ. Sci.* **11**, 842–849 (2017).

704 67. U.S. EPA (Environmental Protection Agency). *Framework for Metals Risk Assessment*.
705 (2007).

706 68. Boyle, D., Catarino, A. I., Clark, N. J. & Henry, T. B. Polyvinyl chloride (PVC) plastic
707 fragments release Pb additives that are bioavailable in zebrafish. *Environ. Pollut.* **263**,
708 114422 (2020).

709 69. Caporale, N. *et al.* From cohorts to molecules: Adverse impacts of endocrine disrupting
710 mixtures. *Science (80-.).* **375**, (2022).

711 70. Rudel, R. A., Camann, D. E., Spengler, J. D., Korn, L. R. & Brody, J. G. Phthalates,
712 Alkylphenols, Pesticides, Polybrominated Diphenyl Ethers, and Other Endocrine-
713 Disrupting Compounds in Indoor Air and Dust. *Environ. Sci. Technol.* **37**, 4543–4553
714 (2003).

715 71. Fromme, H. *et al.* Non-phthalate plasticizers in German daycare centers and human

biomonitoring of DINCH metabolites in children attending the centers (LUPE 3). *Int. J. Hyg. Environ. Health* **219**, 33–39 (2016).

72. Nagorka, R., Conrad, A., Scheller, C., Süßenbach, B. & Moriske, H. J. Diisononyl 1,2-cyclohexanedicarboxylic acid (DINCH) and Di(2-ethylhexyl) terephthalate (DEHT) in indoor dust samples: Concentration and analytical problems. *Int. J. Hyg. Environ. Health* **214**, 26–35 (2011).

73. Larsson, K. *et al.* Phthalates, non-phthalate plasticizers and bisphenols in Swedish preschool dust in relation to children's exposure. *Environ. Int.* **102**, 114–124 (2017).

74. Fréry, N. *et al.* Biomonitoring of occupational exposure to phthalates: A systematic review. *Int. J. Hyg. Environ. Health* **229**, 113548 (2020).

75. Just, A. C. *et al.* Vinyl flooring in the home is associated with children's airborne butylbenzyl phthalate and urinary metabolite concentrations. *J. Expo. Sci. Environ. Epidemiol.* **25**, 574–579 (2015).

76. Carlstedt, F., Jönsson, B. A. G. & Bornehag, C. G. PVC flooring is related to human uptake of phthalates in infants. *Indoor Air* **23**, 32–39 (2013).

77. Shu, H. *et al.* PVC flooring at home and uptake of phthalates in pregnant women. *Indoor Air* **29**, 43–54 (2019).

78. Larsson, M. *et al.* PVC - as flooring material - and its association with incident asthma in a Swedish child cohort study. *Indoor Air* **20**, 494–501 (2010).

79. Tuomainen, A., Seuri, M. & Sieppi, A. Indoor air quality and health problems associated with damp floor coverings. *Int. Arch. Occup. Environ. Health* **77**, 222–226 (2004).

80. Bornehag, C. G. & Nanberg, E. Phthalate exposure and asthma in children. *Int. J. Androl.* **33**, 333–345 (2010).

81. Choi, J. *et al.* Associations between building characteristics and children's allergic symptoms - A cross-sectional study on child's health and home in Seoul, South Korea. *Build. Environ.* **75**, 176–181 (2014).

82. Wang, Z. & Praetorius, A. Integrating a Chemicals Perspective into the Global Plastic Treaty. *Environ. Sci. Technol. Lett.* **9**, 1000–1006 (2022).

744 83. Severin, I., Souton, E., Dahbi, L. & Chagnon, M. C. Use of bioassays to assess hazard of
745 food contact material extracts: State of the art. *Food Chem. Toxicol.* **105**, 429–447 (2017).

746 84. Möller, J., Strömberg, E. & Karlsson, S. Comparison of extraction methods for sampling of
747 low molecular compounds in polymers degraded during recycling. *Eur. Polym. J.* **44**, 1583–
748 1593 (2008).

749 85. Deutsch, J. C. Gas chromatographic/mass spectrometric measurement of ascorbic acid
750 degradation in solution. *Methods Enzymol.* **279**, 13–24 (1997).

751 86. European Chemicals Agency (ECHA). SCIP Database. (2020). Available at:
752 https://echa.europa.eu/scip-database.

753 87. United Nations Environment Programme (UNEP), Strategic Approach to International
754 Chemicals Management (SAICM) & Inter-Organization Programme for the sound
755 management of chemicals (IOMC). *The Chemicals in Products (CiP) Programme*. (2015).

756 88. Klotz, M., Haupt, M. & Hellweg, S. Limited utilization options for secondary plastics may
757 restrict their circularity. *Waste Manag.* **141**, 251–270 (2022).

758 89. Wang, Z. & Praetorius, A. Integrating a Chemicals Perspective into the Global Plastic
759 Treaty. *Environ. Sci. Technol. Lett.* (2022). doi:10.1021/acs.estlett.2c00763

760 90. European Comission & European Health and Digital Executive Agency (HaDEA). Digital
761 Product Passport. Available at: https://hadea.ec.europa.eu/calls-proposals/digital-product-
762 passport_en. (Accessed: 16th June 2023)

763 91. Blue Angel - The German Ecolabel & German Environmental Agency. Environmentally
764 Friendly Floor Coverings, Panels, Doors (DE-UZ 176). (2023). Available at:
765 https://www.blauer-engel.de/en/productworld/floor-coverings-panels-doors-made-of-
766 wood. (Accessed: 16th June 2023)

767 92. Blue Angel - The German Ecolabel & German Environmental Agency. The German
768 Ecolabel Low-Emission Floor Coverings , Panels and Doors for Interiors made of Wood and
769 Wood-Based Materials. (2013).

770 93. Freegard, K., Tan, G. & Mortin, R. *Develop a process to separate brominated flame*
771 *retardants from WEEE polymers Interim Report 1 Authors : Business* (2006).

772 94. Klotz, M. & Hellweg, S. Chemical recycling of plastics from a systems perspecitve. (2023).

95. Escher, B. I., Stapleton, H. M. & Schymanski, E. L. Tracking complex mixtures of chemicals in our changing environment. *Science (80-.).* **367**, 388–392 (2020).

SUPPORTING INFORMATION

- Supporting Information File 1 (SI1): Word/PDF file presenting details on methods, additional results (concentration statistics, substance correlations, screening test quality), and additional discussions (exposure to plasticizers)
- Supporting Information File 2 (SI2): Excel file with large tables large tables of processed data. It contains the final analysis results for each sample (Sheet S1), further information on the analytical standards (Sheet S2) and outputs of the different analytical techniques (Sheets S3-S10)
- Supporting Information File 3 (SI3): Zip file containing the protocol used for *ortho*-phthalate quantitation.
- Supporting Information File 4 (SI4): Zip file containing Agilent method files for the GC-MS analyses.
- Supporting Information File 5 (SI5): Zip file containing python scripts for data analysis
- Supporting Information File 6 (SI6): Zip file containing the raw data from all conducted ATR-FTIR measurements, as csv, spa, spc and dx files for each spectrum
- Supporting Information File 7 (SI7): Zip file containing the raw data from all GC-MS ortho-phthalate quantification runs, as Agilent files for each run and Excel files from Masshunter quantification
- Supporting Information File 8 (SI8): Zip file containing the raw data from all GC-MS suspect screening runs, as Agilent files for each run and Excel files from Masshunter identification, Python semi-quantification and substance table