Relevant substitutive/other products/metabolites to be considered

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Authors:	N. Peña, A. Antón, E. Montemayor, C. Basset-Mens, T. Nemecek, P. Fantke
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Contents

Abstract

The present document, Deliverable 2.2, reports Task 2.3. This report shows inorganic PPP (such as copper-based fungicides, potassium phosphonates, ferric phosphate, etc.), metabolites, microorganism and plant-derived compounds, and mineral oils. Although the core focus of the OLCA-Pest project is to assess xenobiotic pesticide active ingredients, we have considered adding other products and related substances that are potentially relevant to be addressed in LCA. This includes coadjutants that might be important for the efficiency of the main active ingredient, as well as other biological treatment products (e.g., PPPs containing *Bacillus thuringiensis*). Besides the developed list, additional information regarding EU regulation status, as well as the allowance in organic farming of the listed compounds is delivered, and guidance and description of proposed approaches for modeling inorganic compounds, biological treatments, and product metabolites are presented.

1. Purpose and overview

The purpose of this document is the development of a list of relevant substances, usually used as plant protection products (PPP), (i.e., substitutes, metabolites, plant or microorganism derived products, among others) for further inclusion in LCA databases (Task 2.3). The development of this list is framed within the objective of work package WP2, to complete, harmonize, and complement LCI and LCIA results for relevant pesticides and related substances that are currently not included in LCA databases.

Most of the selected substances are quite popular in agricultural production and are extensively used in organic farming. However, the lack of characterization factors (CFs) in some cases or the appropriateness for characterizing others (e.g., metals) on one side, and clear recommendations on how to deal with natural and biological treatment products in emission and impact modeling on the other side results in a clear gap for agricultural LCA studies. Therefore, OLCA-Pest aims to provide some guidelines on how to advance for both LCA practitioners and further research.

The developed list of substances that were considered relevant for further inclusion in LCA databases was focused on products used in organic farming (e.g., inorganic and biological substances), substitutes or new products, product metabolites and other products (e.g., coadjutants, carriers, or synergists). The starting point for selecting these additional substances was to screen for PPPs that were prioritized by OLCA-Pest partners and relevant for the development of their WP6-related case studies. As a second step, the main importance was given to inorganics and main product metabolites, as stated in task 2.3 of the OLCA-Pest project. Finally, natural and biological pesticides used in organic farming practices, and other highly used substances were also considered.

Alternative products may be classified in numerous ways. We have considered several of them in order to have a comprehensive list and collect as much information as possible regarding the substance group and nature, the target pest and legislative status, among many other characteristics. First, they were classified into substance groups, adding the type of pesticide according to target pests (see section 2.2.3). Second, additional information regarding EU regulation status, as well as their allowance in organic farming, was also discussed (see section 2.2.4). Finally, in section (2.2.5), some advice/guidance on how to advance in the present gap in LCA modeling of inorganic compounds, biological treatments, and product metabolites are proposed.

2. Relevant substances

The first classification of relevant substitutive substances, metabolites, and other products to be considered has been done according to the substance group and nature of the compound:

- **Inorganic compounds**: Most of the substances listed are inorganic compounds; these compounds can be defined as those who do not contain carbon in its molecule. However, a reduced number of carbon-containing compounds is also considered as inorganic (e.g., carbonates, carbon oxides). Compounds in this group can be further distinguished into sub-groups such as metal and non-metal compounds (Kirchhübel and Fantke 2019). PPP's in this group can include borates, silicates, and sulfur. Many of those minerals are mined from the earth and grounded into fine powders (usually commercialized as wettable powders -WP). Although, nowadays, they can also proceed from recycled materials. Some of these PPPs work as toxic substances and some work by physically interfering with the target pest.
- **Biological pest control**: Biological pest control products are commercially available products that contain beneficial organisms: the naturally occurring enemies of unwanted pests and pathogens. In practice, companies select and proliferate natural enemies and derive these products (e.g., *Bacillus thuringiensis*-Bt). These natural enemies or 'biological control agents' can be viruses, bacteria, fungi or insects (natural predators). Although, the last group (insects) will not be included as part of the ecotoxicity assessment.
- **Micro-organism derived:** They come from naturally occurring or genetically altered bacteria, fungi, algae, viruses or protozoans. Microbial control agents can be effective and used as alternatives to chemical insecticides. A microbial toxin can be defined as a biological toxin material derived from a microorganism, such as a bacterium or a fungus (Canan Usta 2013).
- **Plant-derived**: The secondary compounds of plants are a vast repository of compounds with a wide range of biological activities. Natural insecticides such as pyrethrum, rotenone, and nicotine have been used extensively for insect control. Limonoids such as azadirachtin and gedunin, present in species from *Meliaceae* and *Rutaceae* are recognized for their toxic effects on insects and are used in several insecticide formulations in many parts of the world (Bora et al. 2012).
- **Metabolites**: These substances, known as metabolites or transformation products, are the product of chemical reactions that occur naturally within cells during metabolism. In addition, most pesticides are subject to metabolic degradation in plants or the environment. The resulted metabolite may have different chemical, physical and toxic characteristics, which require a specific characterization factor to assess its potential toxicity impact.
- **Mineral oils:** these compounds are defined as a liquid by-product of the distillation of petroleum. A mineral oil in this sense is a transparent, colorless oil composed mainly of alkanes and cyclic paraffin's.
- **Adjuvant/synergist**: These are chemical substances added to the pesticide formulation in order to improve the efficiency of the pesticide.
- **Other products**: In this group, the remaining products that we were not able to classify into one of the above groups have been pooled together, thus representing a miscellaneous collection of substances (e.g., elements- metal and nonmetal, coating agents or amides) or unclassified substances.

Alternative products were further classified according to the target group of organisms: acaricide, algicide, attractant, bactericide, elicitor, fungicide, herbicide, insecticide, molluscicide, nematicide, plant grow regulator, repellant, rodenticide, virus inoculation, and wood preserving. Table 1 shows the list of the relevant substances classified according to the substance group of the product as well as its target pest.

Table 1: ***List of relevant substances and pesticide categories (AC acaricide, AL algicide, AT attractant, BA bactericide, EL elicitor, FU fungicide, HB herbicide, IN insecticide, MO molluscicide, NE nematicide, PGR plant grow regulator, RE repellant, RO rodenticide, VI virus inoculation, and WP wood preserving)***

CAS-RN	Substance Name	Pesticide Category
	Inorganic compound	
8011-63-0	Bordeaux mixture	FU
1305-62-0	Calcium hydroxide	IN, FU, HB
1344-81-6	Calcium polysulfide (Lime sulfur)	FU
124-38-9	Carbon dioxide	IN, RO
23087-46-9	Copper ammonium acetate	FU
1344-69-0	Copper hydroxide	FU
142-71-2	Copper of Copper acetate (anhydre)	FU
6046-93-1	Copper of Copper acetate (monohydrate)	FU
1184-64-1	Copper of Copper carbonate	FU
1317-39-1	Copper (I) oxide Cu2O	FU
1332-40-7	Copper oxychloride	FU
1317-38-0	Copper (II) Oxide CuO	BA, FU
7758-98-7	Copper Sulfate	FU, AL, BA
7758-99-8	Copper Sulfate Pentahydrate	IN, HB
12280-03-4	Disodium octaborate tetrahydrate	WP
10045-86-0	Ferric phosphate (anhydrous)	MO
7785-87-7	Manganese(II) sulfate monohydrate	FU
13092-66-5	Magnesium Phosphate (anhydre)	n/a
7664-38-2	Phosphoric acid	n/a
13492-26-7	Potassium phosphite	FU
13977-65-6	Potassium phosphonates	FU
7704-34-9	Sulfur	FU, AC, RE
12527-76-3	Tribasic copper sulfate	FU
57-13-6	Urea	FU, IN, WP
7446-19-7	Zinc sulfate monohydrate	FU

CAS-RN	Substance Name	Pesticide Category
	Biological pest control	
n/a	Bacillus thuringiensis (Bt)	IN, BA
n/a	Bt Aizawai strains ABTS-1857 and GC-91	IN, BA
n/a	Bt Israeliensis (serotype H-14) strain AM65-52	IN, BA
n/a	Bt Kurstaki strains ABTS 351, PB 54, SA 11, SA12 and EG 2348	IN, BA
n/a	Bt Tenebrionis strain NB 176 (TM 14 1)	IN, BA
n/a	Marine algae	n/a
n/a	Neoseiulus cucumeris	IN
n/a	Pseudomonas sp Strain DSMZ 13134	FU
n/a	Rhizobium meliloti	n/a
n/a	Trichoderma asperellum strain ICC012	FU
n/a	Trichoderma asperellum strain T11	FU
n/a	Trichoderma asperellum strain T25	FU
n/a	Trichoderma asperellum strain T34	FU
n/a	Trichoderma harzianum strain ITEM 908	FU
n/a	Virus de la granulose	VI
	Micro-organism derived	
119791-41-2	Emamectin	IN
77-06-5	Gibberellic acid	PG
19408-46-9	Kasugamicina	FU, BA
168316-95-8	Spinosad	IN
	Plant derived	
11141-17-6	Azadirachtin	IN
8008-56-8	Lemon oil	IN
8028-48-6	Orange oil	IN
8003-34-7	Pyrethrin	IN, AC
8008-57-9	Sweet orange peel oil	IN, RE
8016-84-0	Tagetes oil	AC, IN
8007-46-3	Thyme oil	IN
	Metabolites	
7664-38-2	Phosphoric acid	n/a
210880-92-5	clothianidin	IN, Metabolite
100-51-6	Benzyl alcohol	Metabolite
149878-40-0	Diazene	Metabolite
526224-31-7	IN-KG433	Metabolite

CAS-RN	Substance Name	Pesticide Category
	Mineral oils	
8002-05-9	Petroleum oil	FU, HB, IN, AC
8012-95-1	Paraffin oil	AC, IN, AD
8042-47-5	Vaseline oil (paraffin oil)	IN, AC
	Adjuvants/synergists products	
13397-24-5	Calcium sulphate (gypsum)	n/a
29848-79-1	Metil palmitat	n/a
51-03-6	Piperonyl butoxide	n/a
	Others	
68439-50-9	Alcohols C12-14, ethoxylated	n/a
113614-08-7	Beflubutamid	HB
7440-42-8	Boron	FU, IN,
9012-76-4	Chitosan hydrochloride	EL (FU, BA)
624-92-0	Dimethyldisulfide	FU, HB, IN, NE
55774-32-8	(E,Z)-7,9-Dodecadien-1-yl acetate	AT
900-95-8	Fentin acetate	FU, MO, AL
185119-76-0	Iodosulfuron	HB
7439-89-6	Iron	n/a
1332-58-7	Kaolin	IN
61790-53-2	Kieselgur (diatomaceous earth)	IN, AC,
7439-96-5	Manganese	n/a
n/a	Natural polysaccharides	n/a
127277-53-6	Prohexadione-calcium	PG
298-14-6	Potassium hydrogen carbonate	n/a
7440-21-3	Silicon	IN, AC
n/a	Synthetic latex	n/a
67892-35-7	Verticillium lecanii	IN
7440-66-6	Zinc	FU

Further information on substance groups, approval status under organic and conventional European regulation, categorization and inclusion in the case studies (described in WP6 and D6.1) of the OLCA-Pest project, is summarized in the supplementary electronic material.

3. EU legislation

A plant protection product usually contains more than one component. The active component that acts against pests/plant diseases is called the "active substance." The Commission evaluates every active substance for its safety before it reaches the market as a PPP. Substances must be proven safe for people's health, including their residues in food, and effects on animal health and the environment.

As the OLCA-Pest project is set in a European context, information on the status under EU regulation is provided (see supplementary electronic material). However, as far as practitioners may be interested, the list of substances included in this document also contains some substances extensively used in agricultural production, that are currently not approved in EU legislation.

In the case of biopesticides, the EU commission also regulates them; however, there is no applicable toxicity data. In addition, we have provided information on the status under the regulation for organic agriculture, where a strict list of substances and compounds is approved.

4. Current proposed approaches, considerations for guidance and further research

In the following, proposed methods to address the selected relevant substitutive substances, metabolites and other products are summarized in the context of LCA. These proposed approaches could be the base to build further guidance in the OLCA-Pest project.

- **Inorganic compounds**:

Kirchhübel and Fantke (2019) provide initial guidance to classify and characterize toxicity related impacts of inorganic substances. The classification criteria include six levels of refinement for chemical substances (substances included in this document where classified up to the forth level of the proposed classification system). This classification method of common physicochemical properties can be used to determine similar environmental pathways and mechanisms to be considered and to define how the fate, exposure and effects of inorganic compounds can be adequately modeled. Specifically:

- For environmental **fate** some of the identified drivers for inorganic substances include chemical reaction kinetics and dynamics, such as hydration, hydrolyzation, or pH dependent reactions. In this regard, the authors recommend to include the formation of all relevant reaction products of an emitted substance in all compartments by modelling all involved processes (such as oxidation, complexation, precipitation and degradation).
- For modelling **exposure** of organisms, in the case of ecotoxicity, bioavailability is a crucial factor to be considered. Furthermore, interaction of inorganic compounds with the receiving compartments (e.g., soil) and their characteristics (e.g., pH), and, in some cases between chemicals, may be relevant to consider when characterizing these compounds.
- For toxicity **effects,** it is also a function of the compound's complex reactions. Therefore, relevant and predominant reaction products are required when modelling the effect factor characterization and need to be combined with the product's corresponding fractions.

- **Guidance and considerations for copper-based fungicides**:

For emission modelling a primary distribution of emissions is recommended. This primary distribution will be quantified based on the total metal content within the active ingredient studied (this information is available on the label of the product, in the material safety data sheet or in the register for phytosanitary products at national level, e.g., copper oxychloride with total copper content of 35%).

For toxicity evaluation it is recommended to characterize copper-based fungicides (i.e. Bordeaux mixture, copper hydroxide, copper oxychloride, to name some) with the CF for copper cation Cu (II) provided in USEtox 2.02 (or following versions), as this is the prevalent species in all related fungicides and the metal ion is considered the relevant part causing toxicity to organisms. Furthermore, USEtox already includes a bioavailability factor in the calculation of the CF for Cu(II), which is the fraction is the fraction between bioavailable metal and total metal concentration (Dong et al. 2014).

- **Metabolites:**

van Zelm et al. (2010) propose a framework for the inclusion of transformation products (i.e., metabolites) in the LCIA by including them in the calculation of CFs. In this framework, persistence, mobility, and toxicity of metabolites are addressed together with their parent compounds to calculate the CFs. By including up to four generations of metabolites of each parent compound and also integrating an algorithm that approximates the effect of intermittent rain events, the **fate** factor was calculated. Furthermore, **effect** factors were calculated according to the nonlinear multi-substance potentially affected fraction of species (msPAF) method, which explicitly accounts for the nonlinearity in concentration-response relationships. Although the results are highly uncertain, it was demonstrated for several chemicals that the exclusion of metabolites can lead to groundless conclusions concerning the life cycle impacts for freshwater ecotoxicity of those chemicals.

Main topics for **further research** that are beyond the scope of OLCA-Pest project are the inclusion of a framework both in the emission modelling and impact characterization, and also for the manufacturing process for inorganic substances such as Sulphur and biological pest control .

5. References

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