Don’t mix the grape and the grain: are ERA official procedures suitable for inorganic plant protection products?

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INTRODUCTION

In numerical terms, natural inorganic compounds represent a small minority of active ingredients used in Plant Protection Products (PPP). In spite of this, their usage is extremely widespread. This work tries to assess to which extent ERA PPP EU official procedures (conceived mainly for organic xenobiotics), are suitable for describing the environmental fate and the related effects on non-target organisms of natural inorganic substances, using copper as a case study.

SOIL

- Since copper does not degrade, the standard modelling approach (DT_{50}–based) is not able to predict actual dissipation times in soil.
- Scenarios considering applications over several years result in a linear accumulation of copper, with no plateau. However, monitoring data (Fig.1) in soils where copper has been applied for many years (up to a century) challenge the linear accumulation hypothesis.
- Until suitable models are made available and become widely accepted, risk assessment should pose more emphasis on monitoring data. A review of about 55 studies (Fig.1) shows that PEC proposed by EFSA[1] are higher than 80% of measured concentrations (median/mean values) representing worst-case scenarios (established vineyards).
- Suitable predictive models should consider realistic environmental scenarios, in order to embrace a complex system of trade-offs. A conceptual model for upper soil layers (where copper is usually concentrated) is proposed in Figure 2.

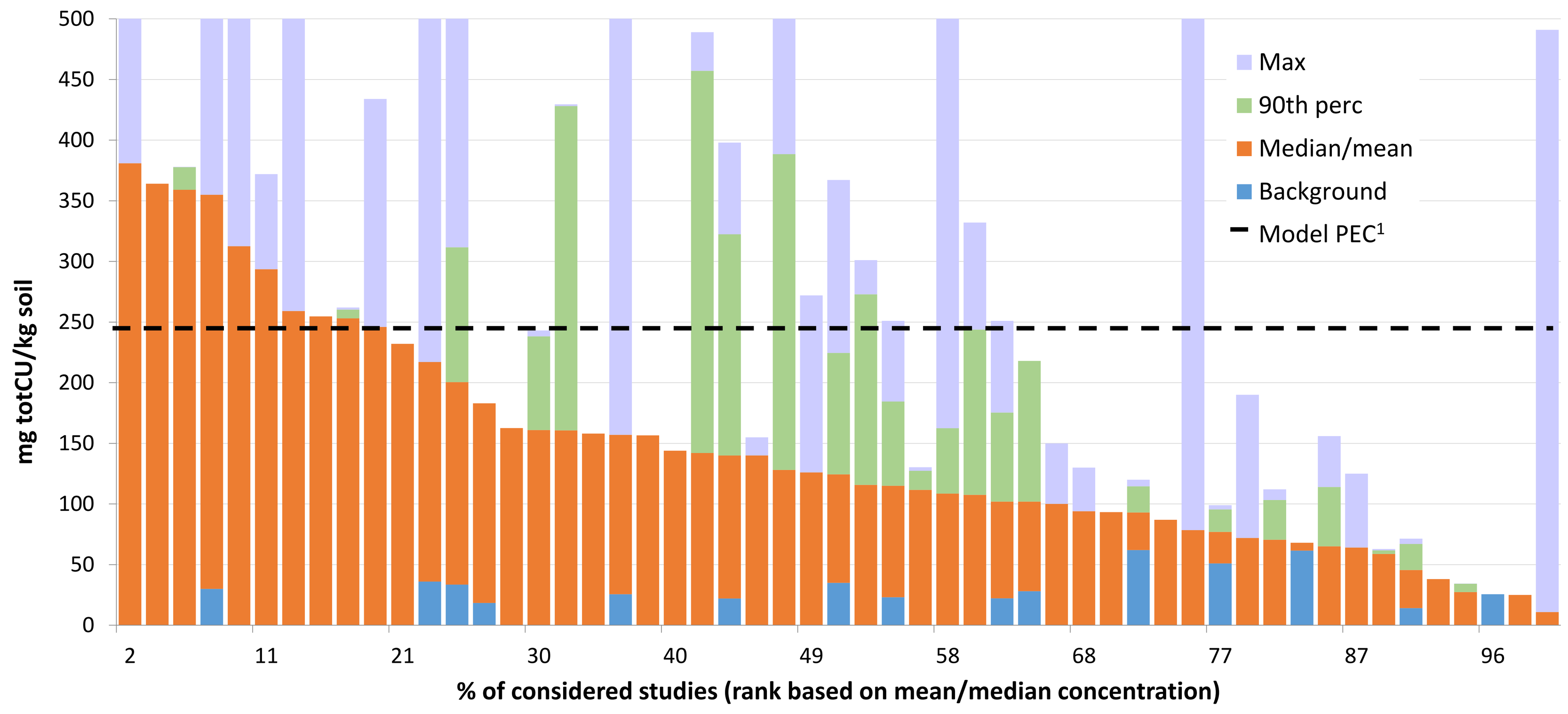
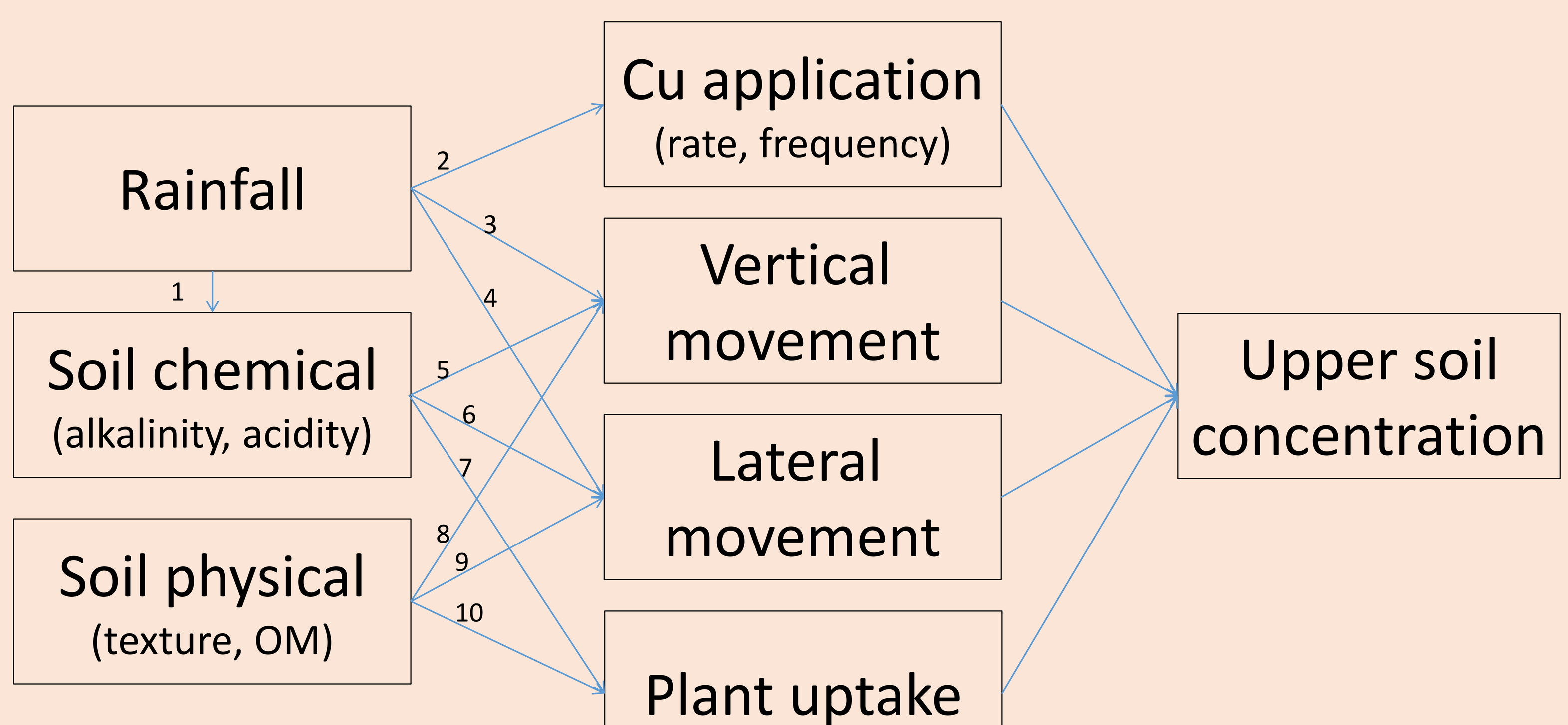


Fig. 1: Comparison between the PEC estimated by EFSA[1] (dashed line – 20 years application of 8 kg Cu*ha⁻¹*y⁻¹+ background concentration of 32 mg Cu/kg) and upper soil concentrations reported in literature for established vineyards in 17 European countries (28% Spain, 25% France, 11% Italy, other countries < 10%).



Process #	Description
1	Excess rainfall leaches base cations from the soil, decreasing soil pH.
2	High rainfall cause a favourable environment for fungi, therefore increasing the need for more fungicides (i.e. copper) input.
3	Free copper ion can be transported to deeper soil layers under the effect of water leaching.
4	Water surface runoff can transport copper both in solution (rare) or by means of soil particles erosion (more common).
5/6/7	Chemical properties of soil influence the speciation of copper. E.g. high acidity cause the formation of copper free ion, which is more mobile in soil (vertical and lateral movement), and bioavailable for plants.
8/9	Sandy soils with poor organic matter content can not strongly bind copper, making movements to deeper soil horizons more likely. On the contrary, when copper is strongly bounded in the upper soil layer, storm water can transport a greater amount of copper by erosion.
10	Texture and organic content of soil influence the adsorption/complexation of copper, determining together with chemical properties the amount of bioavailable copper.

Fig. 2: Conceptual model summarising the most influencing factors to be considered when predicting copper concentration in agricultural soils due to fungicide applications. A detailed description of the relevant processes is given in the table on the right.

SURFACE WATERS

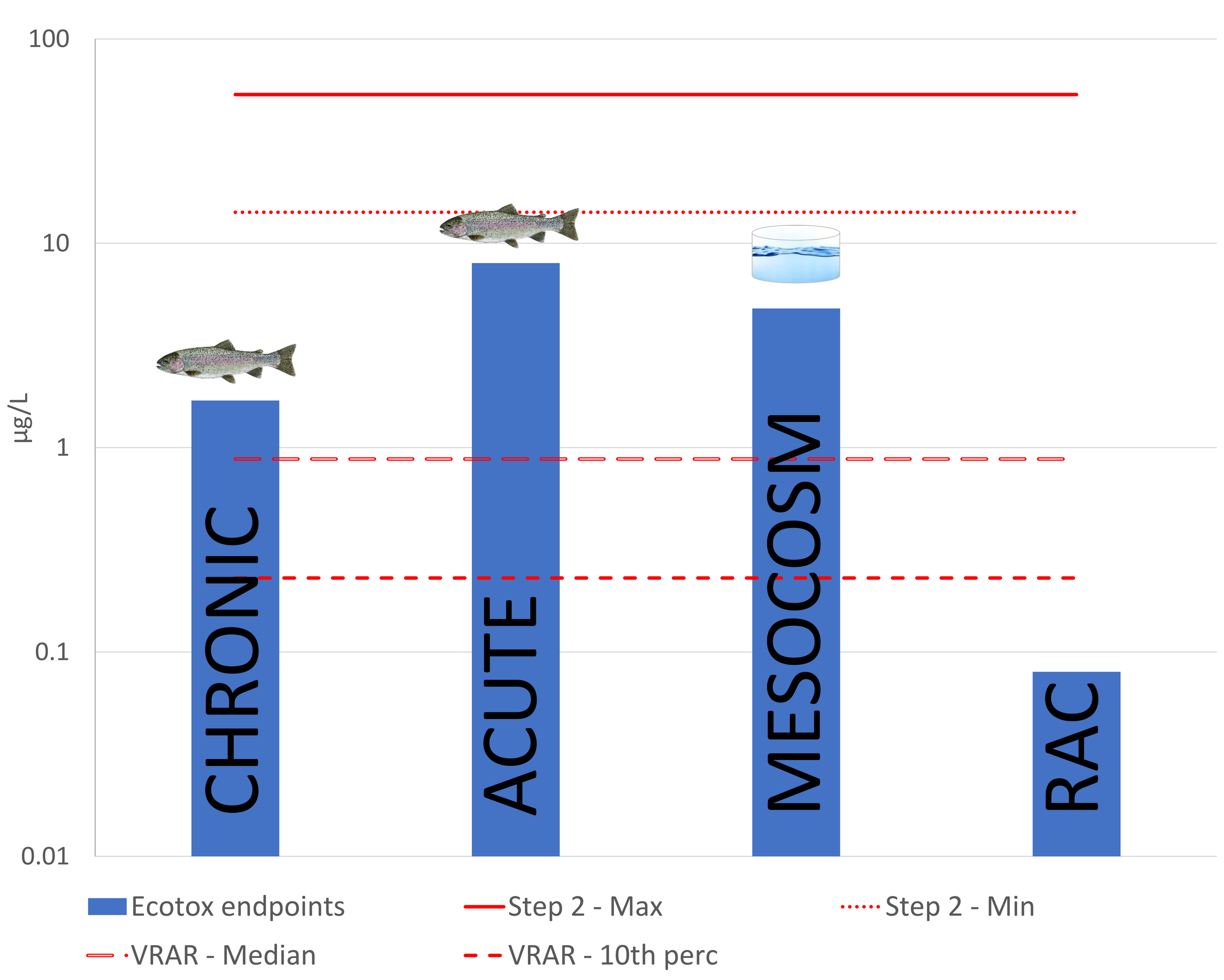


Fig. 3: Comparison between ecotoxicological endpoints, RAC, PEC ranges (derived with FOCUS Step 2), and copper concentrations measured in relatively pristine water bodies (VRAR)[2].

- FOCUS models used at step 3 were considered inappropriate for the PEC assessment of copper compounds. Risk assessment was carried out considering Step 2 PEC estimation[1].
- PEC estimated at step 2 are well above all relevant ecotoxicological endpoints without considering any safety factor. PECs are very likeky to be highly overestimated.
- The calculated RAC is 11 times lower than the median copper concentration measured in relatively pristine water bodies across Europe (VRAR)[2]. 90% of measurements in those water bodies present a copper concentration at least 3 timer higher than the RAC.
- The use of large assessment factors is not a suitable approach for natural compound such as copper, because it leads to unrealistic concentrations.
- Since a great amount of aquatic ecotoxicity tests is available in the literature, these data can be screened for reliability and used to reduce the uncertainty due to inter-species variability and acute-to-chronic extrapolation.
- Biotic Ligand Models (BLM) estimate bioavailability and organisms sensitivity to inorganic compounds, both based on the influence of environmental parameters.
- An extensive review of ecotoxicity data using BLMs was already performed in the VRAR[2], where a worst case HC_5 based on chronic NOEC values was set at 7.8 µg/L.

PERSPECTIVES IN REGULATORY-ORIENTED RESEARCH

- There is a strong need for widely accepted models able to predict the environmental fate of inorganic compounds used in PPP, and their bioavailabiliy. Meanwhile, a management optimisation of available monitoring data into database at EU level would greatly help the risk assessment process.
- Integration of TK/TD models with BLM: most of current BLMs are based on the idea that toxicity depend mainly upon surface accumulation to biotic ligands, however it has been already proven (at least for mammals) that organisms have the ability to regulate internal copper concentration through homeostatic mechanisms.
- Future approaches should account for adaptative mechanisms, both at individual level (especially vertebrates) and at population level (invertebrates).

REFERENCES

[1] European Food Safety Authority (EFSA), 2013. Conclusion on the peer review of the pesticide risk assessment of confirmatory data submitted for the active substance Copper (I), copper (II) variants namely copper hydroxide, copper oxychloride, tribasic copper sulfate, copper (I) oxide, Bordeaux mixture. EFSA Journal 2013;11(6):3235, 40 pp. doi:10.2903/j.efsa.2013.3235.
[2] European Copper Institute (ECI), 2008. Voluntary risk assessment of copper, copper ii sulphate pentahydrate, copper(i)oxide, copper(ii)oxide, di-copper chloride trihydroxide.