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Pesticides in Agricultural Soils: Major Findings from Various Monitoring Campaigns in Switzerland

Thomas D. Bucheli^{*a}, Elias Barmettler^b, Nora Bartolomé^{ac}, Isabel Hilber^a, Karel Hornak^a, Reto G. Meuli^d, Vanessa Reininger^d, Judith Riedo^{bdef}, Andrea Rösch^a, Philipp Sutter^a, Marcel G.A. van der Heijden^{bg}, Daniel Wächter^{dh}, and Florian Walder^{bf}

Abstract: Synthetic pesticides are widely applied in modern agriculture, where they are used against diseases, pests, and weeds to secure crop yield and quality. However, their intensive application has led to widespread contamination of the environment, including soils. Due to their inherent toxicity, they might pose a risk to soil health by causing harm to non-target organisms and disrupting ecosystem services in both agricultural and other exposed soils. Following the Swiss National Action Plan on the reduction of pesticide risks, Agroscope has conducted several soil monitoring studies that are briefly presented here. All of them resort to different multi-residue trace analytical approaches to simultaneously quantify up to about 150 modern pesticides by either accelerated solvent, or Quick, Easy, Cheap, Efficient, Rugged, Safe (QuEChERS) extraction, followed by separation and detection with liquid chromatography-triple quadrupole mass spectrometry. While partly still in progress, our investigations led to the following major findings thus far: Multiple pesticides are commonly present in soils, with individual concentrations in agricultural soils often reaching up to a few tens of µg/kg. Pesticide occurrence and concentrations in agricultural soils primarily depend on land use, land use history and cultivated crops. Pesticides can prevail much longer than predicted by their half-lives and were found in soils even decades after conversion from conventional to organic farming. Corresponding residual fractions can be in the order of a few percent of the originally applied amounts. We further found negative associations of pesticide residues with the abundance of beneficial soil life, underpinning their potential risk to the fertility of agricultural soils. Traces of pesticides are also detected in soils to which they were never applied, indicating contamination, e.g. via spray drift or atmospheric deposition. These results confirm the general notion of both scientists and legislators that prospective risk assessments (RA; as executed during registration and use authorization) should be confirmed and adjusted by retrospective RA (e.g. by environmental monitoring studies of currently used compounds) to jointly lead to an overall reduced environmental risk of pesticides.

Keywords: Micropollutants · Plant protection products · Swiss National Soil Monitoring Program



Thomas D. Bucheli leads the research group Environmental Analytics at Agroscope, the Swiss Centre of Excellence for Agricultural Research, where he investigates the occurrence, fate, and behavior of organic chemicals in the agro-environment. His current focus is on natural toxins, pesticides, plastics, biochar, and related occurrence, sorption, and bioavailability studies. He is a lecturer at the Swiss Federal Insti-

tute of Technology, a Board Member of the Swiss Chemical Society's Section Chemistry and the Environment, the Swiss Delegate to the European Chemical Society's Division Chemistry and the Environment, and an editor of the Springer Journal Environmental Science and Pollution Research.



Elias Barmettler did his Masters in Agricultural Sciences at ETH Zurich. He now works as a PhD candidate at the University of Zurich and Agroscope, where he studies pesticide residues in vineyard soils and their effects on soil microbial communities.



Nora Bartolomé completed her PhD at ETH and Agroscope (2013–2019), focusing on passive soil sampling methods for detecting polycyclic aromatic hydrocarbons contamination. Following her PhD, she furthered her research in passive sampling method development and monitoring for pesticide compounds in soil, water and sediments through several postdoctoral positions (2019-2021) at Universidad de Here-

dia (Costa Rica), Stanford University (USA), and return to Agro-

^{*}Correspondence: Dr. T. D. Buchelia, E-mail: thomas.bucheli@agroscope.admin.ch

^aAgroscope, Environmental Analytics, Reckenholzstrasse 191, CH-8046 Zürich; ^bAgroscope, Plant-Soil Interactions; ^cEMPA. St. Gallen; ^dAgroscope, NABO; ^eFreie Universität Berlin, Department of Biology, Chemistry and Pharmacy; ^fAgroscope, Soil Quality and Soil Use; ^gUniversity of Zürich; ^bSwiss Competence Center for Soil, University of Applied Sciences, Zollikofen

scope (Switzerland). Since 2021, she is working as scientific collaborator in the Technology and Society Lab at Empa in St Gallen.



Isabel Hilber has been working as a researcher at Agroscope since 2009. Topics she has been focusing on are organic pollutants such as pesticides, PAHs, and PCBs in soil or biochar. Collaboration with researchers from Cuba, Pakistan, and Poland formed the main part of her work. From 2005 to 2008 she was a PhD student at the Research Institute for Organic Agriculture (IFiBL) and from 1999–2005 a student of

Environmental Sciences at ETHZ.



Karel Hornak studied biology and limnology at the University of South Bohemia (Czech Republic). He holds a PhD in aquatic sciences, examining trophic interactions among aquatic bacteria, protists and viruses. He then moved to Switzerland to study the fate and transformation of natural dissolved organic compounds at the University of Zürich. In 2022, he joined the Environmental Analytics group at Agroscope

where he is currently investigating the behavior of pesticides in the environment.



Reto G. Meuli is a physical geographer specialized in soil science. After receiving his PhD from ETH Zurich in 1997, he worked as a soil- and contaminated site specialist in Switzerland. From 2008 to 2023, he was the head of the research group 'Swiss Soil Monitoring Network (NABO)' at the Agroscope. He was also a board member of the Soil Science Society of Switzerland (2010–2022), of which he was President in 2012–2014.



Vanessa Reininger works at NABO in the Soil Quality and Soil Use group at Agroscope. Vanessa is responsible for measure 3.6.6.7 within the Swiss National Action Plan on the reduction of pesticide risks (AP PSM) – the development of a pesticide monitoring for agriculturally used soils in Switzerland. This includes pre-studies, cooperation with farmers for site acquisition all over Switzerland, leading to a pesticide routine monitoring.



Judith Riedo received her PhD from the University of Zurich in 2022, where she studied the occurrence of pesticides in soils and their impact on soil microorganisms at Agroscope. Her current research as a postdoc at the Freie Universität Berlin focuses on the effects of pesticides and other environmental stressors on beneficial soil micro-organisms.



Andrea Rösch is an environmental scientist working on analytical method development to determine the occurrence and fate of organic pollutants in different environmental compartments such as water and soil.



Philipp Sutter holds a Federal Vocational Education and Training (VET) Diploma as chemical laboratory technician. He executes multiresidue pesticide analyses for the AP PSM as described in this article.



Marcel G.A. Van der Heijden leads the research group Plant–Soil Interactions at Agroscope, and he is professor for Agroecology and Plant-Microbiome Interactions at the University of Zurich and Professor for Mycorrhizal Ecology at Utrecht University in the Netherlands. His current research focuses on plant-microbiome interactions, the development of sustainable farming practices including organic agriculture.

With his team, he tests the impact of pesticides and soil stressors on soil microbes and mycorrhizal fungi. He is currently President of the International Mycorrhiza.



Daniel Wächter holds an engineer (FH) degree in Environmental Engineering from the University of Applied Sciences (ZHAW). He recently transitioned to a role as a Data Management Specialist at the Swiss Competence Center for Soil (KO-BO), part of the Bern University of Applied Sciences, starting in August 2023. Prior to this, he worked at Agroscope, where he was responsible for quality assurance within the

Swiss Soil Monitoring program.



Florian Walder is head of the Soil Quality & Use research group at Agroscope and interested in the interactions between soil biology, chemistry and physics and the resulting implications for soil functioning under agricultural management. He has held various positions ranging from postdoc to team leader at Agroscope, but also served as program lead for specialty crops in the research group for fungicide resistance at

Syngenta Crop Protection. Florian Walder earned his PhD from the University of Basel, where he studied the exchange of carbon and soil nutrients between plants and soil through mycorrhizal networks.

1. Introduction

The use of synthetic pesticides in agriculture has played a crucial role in increasing agricultural productivity and ensuring food security.^[1] Pesticides, which can be either natural or synthetic chemicals, are used to control pests, weeds and diseases in plants. Their effectiveness in controlling agricultural pests

has made them an integral part of modern agricultural practices. However, the great success of pesticides has led to their heavy and frequent use, resulting in ever-increasing application rates.^[2] Unfortunately, this intensive use has resulted in widespread contamination of the environment, with adverse effects observed in various ecosystems, including insects, birds, freshwater systems, soils and ultimately humans.^[3–6] As a result, there has been growing public concern about the potential harm caused by pesticides. In response to these concerns, authorities and decision makers around the world, including the Swiss government, have taken action to reduce the risks posed by pesticides to their populations.

Based on the report in fulfilment of the postulate 12.3299 'Needs assessment of an action plan for risk reduction and sustainable use of plant protection products', the Federal Council has instructed several Federal Departments to establish a corresponding action plan (AP PSM), which was adopted as by September 6, 2017.^[7] Its main goals are to reduce the current risks of pesticides by 50% and to render their applications more sustainable. To meet these objectives, an array of over 50 measures that concern applications, specific risks and supporting tools were defined and implemented. With respect to soil, the overarching goal is that pesticide applications must not lead to long-term negative effects on soil fertility and that the application of pesticides with high risk potential is reduced. Therefore, indicators of soil fertility need to be established, and residues of relevant pesticides and their transformation products in soils have to be identified and monitored, as one way to control that application of persistent pesticides (half-lives > 6 months) is reduced by 50% until 2027. To this end, the Swiss Soil Monitoring Network (NABO) and Agroscope's research group Environmental Analytics are mandated to develop a pesticide residue soil monitoring and corresponding multi-residue trace analytical methodologies, respectively, for the AP PSM (Measure 6.3.3.7).^[7] Even earlier, Agroscope established an internal development programme to support research on indicators of soil fertility. This overview article summarizes some major findings related to fate, behavior and effects of pesticides in soil.

2. Material and Methods

2.1 Pesticides Potentially Relevant for Soil

For our initial projects,^[8–10] 46 pesticides were selected based on their frequency of application within the NABO monitoring network, their predicted environmental concentrations and their expected dissipation rates (DT_{50}), as well as their analytical feasibility for integration into a multi-residue method. Due to the gener-

ally very large variety of active ingredients used, and the foreseen expansion of the monitoring network within the AP PSM, a second method was developed including close to 150 pesticides.[11] The systematic inclusion of as many as possible potentially soil relevant pesticide target analytes is schematically presented in Fig. 1. We started off with a complete list of pesticides (including biological controls, inorganic agents, as well as synthetic compounds) that were registered as plant protection products in Switzerland mainly between 2012 and 2019 (~2700 candidates). They were first filtered using amounts and frequencies of applications in Switzerland, as well as some general chemical-physical properties relevant for distribution into soil, and terrestrial ecotoxicological endpoints. Applying a scoring system elaborated in collaboration with authorities and experts in the field, a shortlist of 145 candidate analytes relevant for long-term soil monitoring was identified. A number of them then had to be excluded as they did not meet the analytical criteria imposed by the envisaged liquid chromatography-mass spectrometry instrumentation. Finally, for reasons of comparability with the earlier method^[8] and specific requests by some experts, 26 further analytes were included, resulting in a total of 146 target analytes. For further details see Rösch *et al.*^[11]

2.2 Soil Monitoring Networks and Soil Sampling

If not specified elsewhere, the results presented below are obtained from the following soil monitoring networks: 1) The NABO routine monitoring network, which operates more than 100 longterm monitoring sites across Switzerland;^[10] 2) an arable farming network with 60 fields in northeast and southwest Switzerland, with different management systems (conventional tillage, conventional without soil tillage, and organic), combined with a vegetable farming network with 40 fields under conventional or organic management, also including 20 additional extensively managed grasslands nearby in eastern Switzerland;^[8,9] and 3) one to be established as part of the AP PSM.^[12]

In general, sampling took place between 2005–2006 (network 1), 2016 (network 2) and from 2019 onwards (network 3). Soil was sampled from 0 to 10 or 0 to 20 cm, with 2-, or 4-cm augers. Larger numbers of subsamples (20 < n < 25) were pooled into composite samples, air-dried at 40 °C until weight constant, crushed and sieved to <2 mm. Samples were then stored in plastic containers at ambient temperature in the dark. For details, the reader is referred to the corresponding original papers.^[8-11]



Fig. 1. Procedure to identify pesticides relevant for a long-term soil monitoring. For details, including explanations of abbreviations, see Rösch et al.[11]

2.3 Multi-residue Pesticide Analysis

Pesticides were extracted from soils according to two different methods. The first method by Riedo *et al.*^[8] contains 46 pesticides and is based on accelerated solvent extraction consisting of two extraction steps. Firstly, an organic mixture of acetone, methanol and acetonitrile in a ratio of 65:10:25 (% v/v) was employed and secondly, an acidic mixture of acetone and 1% phosphoric acid in Millipore water in a ratio of 70:30 (% v/v) was used. Chemical analysis was carried out by high performance liquid chromatography coupled to a triple quadrupole tandem mass spectrometer using electrospray ionization (HPLC-ESI-MS/MS). Finally, all quantified concentrations were converted to μ g per kg of dry soil. The method limits of quantification (MLOQs) varied between compounds and studies, ranging from 0.064 μ g/kg to 36 μ g/kg for Riedo *et al.*^[8]

The second method was developed by Rösch *et al.*^[11] and covers 146 pesticides. Emphasis was put on (i) rigorous method validation using agricultural field soils with native pesticide residues and an in-house prepared partly-aged reference soil, which contains all target pesticides, (ii) the use and addition of ~100 isotopically labelled analyte analogues (ILIS) before the extraction to be able to compensate for potential analyte losses during extraction and further sample preparation as well as soil specific matrix effects during ESI, and (iii) sample throughput to be applicable for a long-term soil monitoring and to be transferable to private/Cantonal laboratories.

The extraction from soil is based on a quick, easy, cheap, effective, rugged, and safe (QuEChERS) approach (extracting agent: acetonitrile acidified with 2.5% formic acid). Similarly to Riedo et al.,^[8] samples were measured using HPLC-ESI-MS/MS. Quantification was based on matrix-matched internal standard calibration using a blank soil with negligible pesticide concentrations (<MLOQ) largely representative for Swiss agricultural soils. The developed method enables the sensitive (median MLOQ: 0.2 µg/kg dry weight, <0.5 µg/kg for 80% of all analytes) and precise (median inter- and intra-day precision of ~4% based on field soils) quantification of pesticides in soils with varying soil properties $(C_{org}$ content between 1 and 5% and soil pH from 3.6 to 7.4). Trueness was determined based on (i) the partly-aged reference soil (concentrations remained stable during 6 months and were close to the spiked concentration), (ii) relative recoveries of soils spiked with pesticides shortly before the extraction (median relative recovery of 103%) and (iii) the participation in a ring trial (median z-scores close to one). For details on method validation, we refer to Rösch et al.[11]

2.4 Determination of Bioavailability (Truly Dissolved Concentrations)

Truly dissolved aqueous concentrations (C_{free}) of pesticides in soil slurry suspensions (30 g soil in 40 mL Millipore water) were quantified by means of passive samplers (silicone strips spiked with the performance reference compound (PRC) phenanthrene-d10 to assure equilibrium distribution). After 30 days, the strips were recovered, pesticides were extracted with two times 50 mL of acetonitrile (once two nights in the presence of internal standards (d5-atrazine and d11-metolachlor for pesticides and d10-pyrene for the PRC), and once more for one night). The extracts were combined and quantified with GC-MS as described in Bartolomé and Bucheli.^[13]

2.5 Analysis of Association of Pesticide Residues with Microbial Soil Life

Several soil microbial parameters linked to soil fertility were assessed for the arable sites in network 2. Microbial biomass was assessed by chloroform fumigation extraction^[14] and basal respiration by the rate of carbon dioxide production over 24 h.^[15]

We further profiled bacterial and fungal microbiota by amplicon sequencing.^[16] We also included specific indicators related to soil nutrient cycling such as the abundance of arbuscular mycorrhizal fungi in roots and soil by visual root assessment or by soil phospholipid fatty acid analysis,^[17] and the abundance of prokaryotic marker genes related to soil nitrogen cycling.^[16]

To assess the potential effects of pesticide residues on soil microbial parameters across the 60 arable sites, we employed multiple linear regression analyses including hierarchical linear models^[18] and multi-model inference^[19] to compare the association of pedoclimatic conditions, management options (*e.g.* the management system) and pesticide residue concentration with the microbial parameters.

3. Results and Discussion

In the following, we present different main findings of several terminated or ongoing research projects, each with a view to illustrate a specific take-home message, expressed in the corresponding subtitle.

3.1 Short-term Variability of Pesticide Residues is Decisive for Sampling

As one of the first activities within the AP PSM Measure 6.3.3.7, we investigated the short-term temporal variability of 46 pesticides quantified as described in Riedo et al.[8] in three different agricultural cultivation types (one soil each), *i.e.* cropland (primary cultures: potato in 2019, winter wheat in 2020), orchard, and viticulture, to identify in which season to perform soil sampling during routine monitoring. In all three soils, fungicides prevailed over the other pesticide types (Fig. 2). The difference was much more pronounced (\geq one order of magnitude higher concentrations) in the special cultures than in the arable soil, however. Fungicide concentrations were higher by a factor of 2 to 5 in the top five cm, compared to the 5-20 cm layer below, while the other types exhibited more equal concentrations. Concentrations of pesticides remained largely constant over the investigated period of two years in the orchard soil, probably due to the frequent applications of multiple products over large parts of the cultivation period. Fungicides dropped from initially around 400 µg/kg to about 100 µg/kg in the vineyard soil. Potato cultivation resulted in elevated soil concentrations of both fungicides and insecticides in the summer of 2019, whereas insecticides additionally peaked around the harvest of winter wheat in 2020. Temporal changes manifested primarily in the topsoil layer. In summary, long-term (*i.e.* interannual) monitoring will have to take intraannual variability into account. For practical reasons, soil sampling is preferred over the winter period, with dormant vegetation, reduced pest pressure, and fewer agricultural activities, such as no pesticide applications.

3.2 Pesticides Are Almost Ubiquitously Present in (Agricultural) Soils

Fig. 3 presents a compilation of frequently, and at elevated concentrations, observed pesticide residues in different soils of Switzerland based on the method by Riedo *et al.*^[8] including 46 pesticides. Several findings are remarkable. First, hardly any soil was free of pesticides. Even sites where one would not necessarily expect any residues, such as grasslands, contained traces of individual compounds. Second, observed concentrations varied widely from below 1 µg/kg up to 230 µg/kg. Third, concentrations and number of detected pesticides were generally highest in special cultures (*e.g.* orchards or viticulture), and conventional arable or vegetable farming. Corresponding organically managed systems contained fewer pesticides, both in terms of concentrations and numbers of individual active ingredients. Finally, certain pesticides that had widely been used over decades in the past remained as almost ubiquitous residues in nearly any soil. This is illustrated by



Fig. 2. Short-term temporal variability of pesticides in selected agricultural soils in two sampling depths. The concentrations of the 46 individual pesticides are summed for each pesticide type. The grey areas in the plots indicate the preferred period of sampling (late autumn – early spring).

the frequent observations of the herbicide atrazine, and its transformation products atrazine-2-hydroxy, and atrazine-desisopropyl. The use of atrazine was banned in Switzerland over a decade ago, but concentrations in the order of a few tens and a few hundreds of μ g/kg for the parent, and its transformation products, respectively, were the rule rather than the exception. For a more in-depth discussion of the occurrence and prevalent sources of pesticides in Swiss (agricultural) soils, we refer to the original publications.^[8–10]

A first application of the analytical method by Rösch *et al.*,^[11] which covers 146 pesticides, to selected Swiss (agricultural) soils (n = 12) revealed the presence of up to 77 different pesticides over all analyzed sites. Cropland and vegetable sites contained the highest number of different pesticides (n = 37), while grasslands and a municipal park contained only a few (n = 1 to 3), and no pesticides were found in the Swiss national park. The highest individual pesticide concentrations were reached for fungicides and transformation products thereof. On the vegetable site, in particular, individual concentrations of up to 140 µg/kg were quantified.

Overall, our findings in terms of concentration ranges, number of observed residues, and major fate and behavior processes responsible for such exposure are largely in agreement with the published scientific literature.^[20–23]

3.3 Even Modern Pesticides Are Legacy Compounds

While it is generally known that persistent organic pollutants such as organochlorine pesticides will remain for decades in re-

cipient environmental matrices such as soil,^[22,24,25] it is relatively striking to even find residues of more modern, currently used pesticides in such systems for many years, as they were designed and intended to exhibit lower persistence, and registered based on corresponding prospective risk assessments. Fig. 4A illustrates that traces in the order of a few percent of originally applied amounts of non- to moderately-persistent pesticides can be quantified in soils several years after their last applications. Examples include propiconazole, chloridazon, linuron, S-metolachlor, as well as the earlier mentioned atrazine. While all of them exhibit field-derived half-lives (DT₅₀) from 19 to 37 days (geometric mean of values compiled from the literature; for details, see Riedo et al.[10]), residual amounts well above those predicted by corresponding firstorder dissipation models remain in soils for several years. Likewise, organically managed arable or vegetable production systems are confronted with residues of modern pesticides up to 20 years after conversion from conventional agriculture (Fig. 4B).

3.4 Total Contents Might not Be Decisive for Pesticide Risk

The study by Bartolomé and Bucheli^[13] determined both total extractable concentrations and C_{free} (Fig. 5) of a few selected pesticides in different NABO, as well as some Cuban soils. The graph illustrates that while a general positive correlation between the two concentration types is discernible, for some compounds the C_{free} varied less (*e.g.* log 2.0 < epoxiconazole (CH) < 2.2 ng/L)



Fig. 3. Frequently observed pesticides in Swiss (agricultural) soils. Individual columns represent, from left to right, individual soils from orchards (n = 3) and vineyards (n = 3; data from Riedo *et al.*^[10]), arable, vegetable and grassland sites (min, mean, and max. values presented for each category, n = 20; data from Riedo *et al.*^[8,9]).

than their corresponding total concentrations (*e.g.* log 0.7 < epoxiconazole (CH) < 1.3 ug/kg). It remains yet to be investigated which of the two concentrations (see *e.g.* Ortego-Calvo *et al.*^[26]) soil organisms are really exposed to, and thus exert any effect. Riedo *et al.*^[27] compared the short-term variability of microbial effects with both contaminant pools, without any clear dominance of either of the two in terms of observed effects.

3.5 Association between Pesticide Residues and Indicators of Soil Fertility

Robust associations were found between pesticide residues and soil microbial parameters, ranging from sum parameters such as microbial biomass to specific taxa and genes.^[8,16] The inferred effects often exceeded those of other management variables, although they were weak compared to the influence of pedoclimatic variables such as pH or organic carbon content. The patterns observed were generally complex, and associations ranged from positive to negative, suggesting that while some microbes may be harmed by the toxicity of pesticide residues, others may benefit from their presence, for example by using them as an energy source. However, the more specific parameters related to soil nutrient cycling, such as arbuscular mycorrhizal fungi and the marker gene for biological nitrogen fixation (*nifH*), were predominantly negatively associated with several specific compounds as well as the number of pesticide residues present.

The results underpin the potential risk of pesticide residues disrupting microbial soil life and important soil functions such as soil nutrient cycling. Although these findings are based on statistical relationships only, we were able to validate some of the effects through greenhouse experiments, which further highlighted the sensitivity of arbuscular mycorrhizal fungi and nitrogen cycling to pesticide exposure.^[27] Our work provides further evidence that the ubiquitous contamination of agricultural soils poses a risk to soil fertility. However, there is also a need to better understand how these effects translate into soil function (*e.g.* productivity) and relate to other management impacts such as ploughing and mineral fertiliser application. Moreover, pesticide residues in soils may result in long-term exposure to low-dose mixtures of compounds, which is not considered in current risk assessments and may need to be considered in the future.

4. Conclusions and Outlook

Our investigations showed that pesticides are frequently and ubiquitously present in (agricultural) soils. Effects on the soil microbiome and certain soil functions have been observed, but an overall risk assessment for soil fertility remains yet to be es-



Fig. 4. A) Percentages of originally applied pesticide concentrations remaining in soil (adapted from Riedo *et al.*^[10]). B) Number of pesticides remaining in soil after conversion from conventional to organic farming (adapted from Riedo *et al.*^[8]).

tablished, *e.g.* within the framework of the AP PSM (Measure 6.3.3.7). The established multi-residue pesticide method^[11] is currently used in a number of ongoing research projects related to pesticides in vineyards, the PestiRed project and the establishment of a pesticide monitoring network (AP PSM, Measure 6.3.3.7). To facilitate and harmonize similar soil monitoring activities at the Cantonal level, the authors advocate and support the transfer of this method^[11] to private and Cantonal laboratories.



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Fig. 5. Bioavailable (C_{free}) vs. total concentrations (C_{tot}) of selected pesticides in different native or spiked (SP) Swiss (CH) and Cuban (CU) soils, for details, see Bartolomé and Bucheli.^[13]

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