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Prediction of accumulation and leaching of fungicide copper in agricultural soils

Report to the European Copper Task Force (ECTF)

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Contents

1 Introduction

Copper is applied extensively to protect a number of crops, including vines/grapes, citrus and other fruits, against fungal attack. In contrast to biodegradable organic chemicals, metals such as copper cannot be degraded in the environment and so can potentially remain as contaminants in the environment for extended periods of time. Metals can undergo processes such as ‘aging’ in certain environmental compartments, such as soils, that reduce their bioavailability and toxicity, but typically a significant proportion of the metal remains in a potentially bioavailable form for extended periods. There is thus a need to assess the potential ecological risks of the ongoing use of copper as a fungicide.

This study has been commissioned by the European Copper Task Force (ECTF) to assess the potential risks of the current and future use of copper as a fungicide. Using a set of typical copper application rates, and a set of scenarios covering a representative range of soil types across Europe, we have simulated copper accumulation in soils, surface waters and sediments using an intermediate complexity dynamic model (the IDMM) designed specifically for the long term behaviour of metals. Predicted copper concentrations over time have been compared with Predicted No Effect Concentrations for soil, waters and sediments to assess the current potential risks, and the prospects for the future development of risk under a scenario of continued copper application have been assessed.

2 Methods

2.1 Intermediate Dynamic Model for Metals

2.1.1 Soil module

The Intermediate Dynamic Model for Metals (IDMM) is an intermediate complexity model for the simulation of metal accumulation in soils and leaching to surface waters. The model computes metal pools in soils, and leaching fluxes to surface waters, on an annual timestep, in response to metal inputs to the soil surface. Within each soil layer, three metal pools are simulated: dissolved, labile particulate and aged particulate. Particulate metal may be associated either with the soil solids or with solids suspended in the soil porewater. Processes simulated comprise equilibrium solid-solution partitioning of labile metal, exchange of soil-bound metal between labile and aged pools, equilibrium speciation of metal in the soil porewater, removal of metal following uptake into the harvestable parts of crop plants, and weathering of metal from ‘inert’ mineral forms into the labile pool. Two soil layers (topsoil and subsoil) of user-defined depth can be simulated. Water entering the topsoil by precipitation or irrigation can leach either laterally to surface water or vertically to the subsoil layer. From the subsoil layer water may percolate vertically to groundwater or leach to surface water. Metal associated with water percolating to groundwater is considered ‘lost’ from the system. Metal movement within the soil and to surface waters may occur in one of three forms: dissolved metal, labile metal adsorbed to suspended matter in the porewater, and aged metal in suspended matter. Concentrations of suspended matter in the porewater moving within and out of the soil are specified as driving variables. On each annual timestep, labile adsorbed and aged metal pools in each soil layer are calculated. A fuller description of the model is given in a previous report [1].

2.1.2 Surface water and sediment module

In the previous risk assessment of metal inputs to soil using the IDMM[4], PECs for surface water and sediment were calculated by simply taking the annual mean of daily predicted values for dissolved and suspended particulate copper in the waterbody under simulation. While this approach follows the standard EU Risk Assessment practice of considering the sediment contaminant concentration to be equal to that of the suspended sediment, consideration of the long-term dynamics of the system leads to the conclusion that a more complex model that explicitly simulates the transfer of copper to bottom sediments is required. Therefore, the original surface water model has been developed to simulate the dynamics of sediment more realistically than was previously the case.

Surface water dissolved copper, and copper concentrations in freshwater sediments, are calculated by assuming that water leaching from the soil layers (soilflow) enters a waterbody of defined volume, along with a constant baseflow assumed to represent upstream flow and seepage from deep soil and groundwater to surface water. The amount of soilflow varies daily and is input as a driving variable, while the concentration of copper in soilflow is assumed constant over each year. Within each annual timestep, surface water concentrations of metal and suspended particulate matter are computed daily by mixing baseflow and soilflow with the water present in the waterbody. The baseflow is assumed to have a copper concentration of 10^{-10}M and a suspended sediment concentration of 15 mg/l. Redistribution of copper between dissolved, labile particulate and aged particulate forms in the suspended sediment is first calculated using WHAM/Model VI[2] and the kinetic aging model used in the soil model. This step assumes that the organic carbon content of the suspended sediment is 5%, in accordance with EU Risk Assessment guidelines[3]. The loss of suspended sediment particles and associated copper from the water column by settling is then simulated using the fractional settling of suspended sediment on each daily timestep. The fractional settling is calculated daily, from the calculated velocity of water through the waterbody and assuming a particle settling velocity of 1 metre per day; thus, the settling rate varies with the discharge of water from the soil; high discharge will give a lower settling rate. The sediment PEC is taken as the mean concentration of copper (mg/kg dry weight) in the top 5cm of the settled sediment. Fluxes of dissolved and suspended particulate copper in the waterbody outflow are computed assuming the daily outflow to equal the daily inflow.

In application, the surface water model is initially run to steady state (constant sediment copper concentration over time) using the steady state concentrations of copper in the soilflow and the fixed, constant concentration of copper in the baseflow. Following attainment of steady state the model is then run dynamically to simulate change over time. In practice, the steady state copper concentrations in the surface water (dissolved) and sediment varied with the scenario, waterbody and attenuation option used. In order to provide a more consistent basis for assessing the potential risks resulting from copper input over time, the steady state contributions to the copper concentrations were discounted in calculating the PECs. Instead, the predicted increases only in dissolved and sediment copper, resulting from inputs to the soil, were taken. 'Background' concentrations of copper in dissolved form and in sediment were then added to the predicted increases. Concentrations of 0.85 µg l^{-1} dissolved copper and 21 mg kg d.w.$^{-1}$ sediment copper were chosen, based on the findings of the EU copper Voluntary Risk Assessment[6]. These concentrations were preferred to the 'ambient' concentrations in European surface waters and sediments presented in the Risk Assessment, since it is considered unlikely that the waterbodies being simulated would be impacted by anthropogenic inputs other than those simulated, i.e. atmospheric deposition and fertiliser application to the catchment.

In the previous application of the IDMM to metal leaching from agricultural soils, a 'worst case' for metal losses in sediment due to erosion was simulated. This assumed that (i) metal concentrations in eroding soil particles were enriched by a factor of five over the bulk soil metal concentration, and (ii) that particles eroding from the topsoil into vertical drainage to the subsoil are transported to surface water or groundwater in the lateral runoff from the subsoil, rather than being trapped in the subsoil. This simulates the rapid vertical transport of particles in soil pipes or cracks. Metal associated with particles transported into groundwater is assumed to be 'lost' from the system and not considered further. This approach is also adopted in the current work.

2.2 Model application

The IDMM is applied by initially calculating the metal present in the soil (dissolved, labile particulate and aged particulate) under 'pristine' steady state conditions (i.e. where the annual input and output fluxes in each soil layer balance. The model then simulates metal dynamics forward in time from this 'pristine' state, in response to changes in metal inputs (e.g. from atmospheric deposition and application of fertilisers/fungicides), soil pH, and the mass of harvestable plant removed annually.

2.2.1 Modelling scenarios

For this work, the model has been applied to the ten soil-water scenarios used by the FOrum for Co-ordination of pesticide fate models and their USe.(FOCUS) for risk assessment of pesticides[1], and previously used for risk assessment of copper and zinc in animal manures[4]. The characteristics of the soils and surface waters in each scenario are given in Appendix 1. Basic soil characteristics (e.g. site density, pH, organic matter and clay content) are based on measurements at the sites. Surface water characteristics are not based on site measurements, but are interpolated from spatial measurements of surface water quality in the FOREGS geochemical baselines database[5]. Inputs of copper via atmospheric deposition, fertiliser use and application as a fungicide are considered. Temporal patterns of inputs due to atmospheric deposition and fertiliser use previously computed were used in this study. Four application rates of copper as a fungicide were simulated: 2, 4, 6, and 8 kg per hectare per annum. In running the scenarios, it was assumed that all input copper (regardless of source) was fully labile and entered the topsoil, i.e. interception of applied copper by plant surfaces and subsequent removal by harvesting was negligible. In terms of copper entering the soil system, the simulated input rates therefore represent 'worst case' scenarios for the actual field application rates.

The FOCUS scenarios comprise six 'drainage' scenarios D1-D6, and four 'runoff' scenarios R1-R4. Drainage scenarios represent locations where water transfers to surface water are dominated by vertical drainage to drain depth followed by lateral drainage to surface water. Surface runoff and losses to groundwater are minimal. These scenarios were simulated using a topsoil layer of 30cm depth and subsoil extending from 30cm to the drain depth, which varied among scenarios. The two soil layers have their own physicochemical characteristics such as bulk density and porewater pH. Runoff scenarios represent locations Vertical drainage to the subsoil and groundwater occurs, but is assumed not to contribute to metal transport to surface waters. Runoff scenarios were simulated using a topsoil layer

5cm deep and a subsoil layer 25cm deep, both having the same physicochemical characteristics.

Surface water concentrations in the FOCUS scenarios are calculable for up to three types of waterbody: stream, pond and ditch, depending upon the specific scenario. Streams are simulated in scenarios D1, D2, D4, D5 and R1 to R4. Ponds are simulated in scenarios D4, D5 and R1. Ditches are simulated in scenarios D1 to D3 and D6. The three types of waterbody differ in their dimensions, water volume and the daily volume of baseflow entering the system. The larger this volume, the higher the settling rate of suspended sediment and the smaller the loss of metal through surface discharge away from the water body. Ponds have the highest volume (900m^3) followed by ditches and streams (30m^3).

2.2.2 Crops

Each FOCUS scenario has an associated set of crops. For this study, the IDMM was set up to simulate metal removal in the following crops: grapes/vines, apples, oranges, olives and hops. The computation of the annual removal of copper in crops is described in Appendix 2. In practice, initial simulations showed that the choice of crop had a negligible effect on the computed metal concentrations, i.e. metal removal by cropping was essentially identical regardless of the crop simulated. Therefore, for simplicity, all the results presented here are for simulations using apples as the crop, with the exception of scenario D6 where grapes are used (since apples are not a crop listed for this scenario).

2.2.3 Attenuation of runoff

In order to simulate the influence of topsoil runoff attenuation through the use of vegetation strips, the fluxes of water and eroded particles to surface water may be empirically decreased by fixed proportions. In this study, we used three options for attenuation in the runoff scenarios:

- No attenuation;
- Presence of 10m wide vegetation filter strips, reducing water fluxes by 60% and eroded particle fluxes by 85%;
- Presence of 20m wide vegetation filter strips, reducing water fluxes by 80% and eroded particle fluxes by 95%;

The latter two attenuation scenarios are those used by FOCUS to simulate mitigation effects in pesticide risk assessment.

For the drainage scenarios, a scenario of ‘no attenuation’ only was run.

2.3 Risk assessment

The IDMM calculates annual concentrations of metal in the 0-30cm soil layer, in surface waters (dissolved phase) and in the bed sediments of the receiving waterbody. Risks were assessed by comparing modelled concentrations of metals with Predicted No Effect Concentrations (PNECs) The PNECs are listed in Appendix 3.

Soil PNECs were calculated using a Microsoft Excel spreadsheet tool produced by Arche Consulting, Ghent, Belgium. The tool calculates soil PNECs for copper, largely following the methodologies in the copper EU Risk Assessment (RAR)[6]. Fuller details may be found in an earlier report[4].

Site-specific surface water PNECs were calculated using a Microsoft Excel spreadsheet tool produced by Watts & Crane Associates, UK. The tool calculates PNECs using empirical equations fitted to outputs of the tools used to calculate site–specific PNECs in the Cu RAR. The water quality parameters required for PNEC calculation are the pH, calcium and DOC concentrations.

A sediment PNEC was obtained from the EU Copper Risk Assessment. The PNEC is expressed in terms of the concentration of copper per unit mass of organic matter in the sediment. Since in this work the sediments were assumed to all have the same organic matter content of 5%, the PNEC is the same (87 mg kg d.w.$^{-1}$) for all the scenarios.

Soil additions of copper as a fungicide are assumed to start in 2010. Predicted concentrations of copper in the topsoil (0-30cm), surface water (dissolved) and sediment are presented and compared with Predicted No Effect Concentrations for these compartments. The effects of runoff attenuation in runoff-dominated scenarios are also simulated as before.

Characteristics of the exposure scenarios, and the site-specific PNECs used, are given in Appendices 1-3. Three sets of PNECs for dissolved copper in surface waters were used: site-specific values calculated based on the calculation methodology presented in the copper EU Risk Assessment, a 'reasonable worst case' PNEC of 6.8 µg l^{-1} from the same document, and a proposed EU regulatory acceptable concentration (RAC) of 9.5 µg l^{-1}.

3 Results

Initial modelling indicated that removal of copper in crops had a negligible effect on accumulation. Therefore simulations were done with one crop type (apple) for each scenario, with the exception of scenario D6 where grapes were simulated.

Tables of predicted copper concentrations in topsoil, surface water and sediment for the present day and 2020, 2030 and 2060 are given in Appendices 1-3. Charts showing the time trends in copper concentrations are presented in Appendices 4-5 and charts illustrating the influence of attenuation measures on predicted surface waters and sediments in the runoff scenarios are presented in Appendix 9.

The assessment indicated that over the period 2010-2060, copper concentrations increased steadily in response to inputs, with no sign of inputs and outputs to the topsoils balancing (steady state). Since copper is retained strongly by soil, the increase in topsoil concentration at a given point in time in response to input is closely related to the cumulative input to that point.. For a long-term assessment further ageing of soil residues and their availability for run-off/drainage as well as removal by transfer to the base sediment need to be considered further.

3.1 Topsoil concentrations and risks

Predicted concentrations of copper in topsoils do not vary greatly across the scenarios at a given point in time for a given application rate. Variations in the concentrations are due largely to variations in soil bulk density, with soils of lower bulk density tending to have higher copper concentrations. This is due to (i) the strong retention of copper by soil, meaning that variations in loss fluxes across the scenarios are not greatly important for soil accumulation, and (ii) the fact that a lower bulk density soil will tend to show higher concentrations of a strongly retained contaminant, simply because there is less solid matter per unit area to intercept the contaminant.

The site-specific PNEC is a function of the soil pH, organic matter and clay content. Lower PNECs are calculated for soils having low pH and low concentrations of organic matter and clay. So the acidic, low clay soil at D3 is predicted to the most intrinsically sensitive of those simulated here, while the D2 soil, having circumneutral pH and a high clay content, is predicted to be the least intrinsically sensitive.

In the current assessment inputs commence at the present day (taken to be 2010), therefore PNEC exceedence at the present day can only occur in response to the other contamination sources considered (atmospheric deposition and fertiliser application). No exceedence of the PNEC was found at the present day. Nor was any PNEC exceedence predicted for the years 2020 or 2030, regardless of the copper input rate. In 2060, exceedences were predicted in scenarios D3, D4, D6, R1, R2, R3 and R4 in response to an input rate of 8 kg Cu ha^{-1} a^{-1}, in scenarios D3, D4, D6, R1, R3 and R4 in response to an input rate of 6 kg Cu ha^{-1} a^{-1}, and in Scenarios D3, R1 and R4 in response to an input rate of 4 kg Cu ha^{-1} a^{-1}. An input rate of 2 kg Cu ha^{-1} a^{-1} was predicted not to cause PNEC exceedence in any scenario in 2060.

3.2 Surface water concentrations and risks

In contrast to the soils, the pattern of PNEC exceedences for waters varies among scenarios, and among the different waterbodies simulated in each scenario. In part this is due to the wide variation in site-specific PNECs, from 1.3 µg l^{-1} in D6 to 47.0 µg l^{-1} in D4, but is also due to the variation in predicted surface water concentrations. Of the types of waterbody simulated, ponds are the most sensitive and streams the least sensitive, relative to the other types. This reflects the lower flushing rate of ponds compared to ditches and streams, which allows contaminant concentrations in the water column to build up over time in response to continually increasing fluxes from the soil.

The predicted surface water dissolved copper concentrations are assessed against three types of PNEC:

i. Site-specific PNECs calculated using a Microsoft Excel spreadsheet tool produced by Watts & Crane Associates, UK. The tool calculates PNECs using empirical equations fitted to outputs of the tools used to calculate site–specific PNECs in the Cu RAR. The water quality parameters required for PNEC calculation are the pH, calcium and DOC concentrations;
ii. A 'reasonable worst case' PNEC of 6.8 µg l^{-1};
iii. A proposed EU regulatory acceptable concentration (RAC) of 9.5 µg l^{-1}.

No exceedence of any surface water PNEC after 10, 20 or 50 years of application was predicted to occur in scenarios D1 (stream and ditch), D3, D4 (stream and pond), D5 (stream and pond), D6, R1 (stream), R3 or R4. In scenarios D2 (stream and ditch) and R2, exceedences were predicted only after 50 years of application. In both of these scenarios, exceedence of the site-specific PNEC only was predicted, in response to input rates of 6 and 8 kg Cu ha^{-1} a^{-1}. In contrast to the other scenarios, exceedences of the site-specific PNEC were predicted to occur in scenario R1 pond after 10 years of application, in response to input rates of 6 and 8 kg Cu ha^{-1} a^{-1}. After 20 years of application, all input rates were predicted to result in exceedence of the site-specific PNEC and input rates of 6 and 8 kg Cu ha^{-1} a^{-1} were predicted to cause exceedence of the reasonable worst case PNEC. After 50 years of application, input rates of 4, 6 and 8 kg Cu ha^{-1} a^{-1} were predicted to cause exceedence of the reasonable worst case PNEC and the proposed EU RAC on top of the exceedence of the site-specific PNEC in response to all the input rates.

3.2.1 Distribution of copper in surface waters

Appendix 10 shows predicted distributions of copper among its different forms in surface waters, for the year 2030 and an input rate of 8 kg Cu ha^{-1} a^{-1}. The distribution of copper is largely dominated by particulate and dissolved organic matter (DOM)-bound forms although there are some small contributions from inorganic dissolved complexes, particularly in D5, D6 and R1. The proportion of free copper ion is consistently below 0.5%, which is typical for this strongly complexing metal.

The greatest variation in the distribution across the sites is that between the sediment and DOM-bound forms. Sediment bound copper is predicted to vary between 50 and 95% of the total, and DOM-bound copper between 4% and 50%. Since the suspended sediment is assumed to have the same composition in all the scenarios, the distribution of copper between sediment and dissolved organic matter is largely determined by the concentration of DOM (Appendix A, (ii), expressed as dissolved organic carbon). The three scenarios where DOM is highest (D1, D3 and D4) all show a relatively high proportion of copper in the DOM-bound form, and corresponding low proportions of suspended sediment-bound copper.

Predictions of copper distribution were also done for the other loading rates (data not shown). There is negligible influence of loading rate on the predicted distributions.

3.3 Sediment concentrations and risks

The sediment PNEC was not predicted to be exceeded after 50 years of application in response to any input rate. In a number of the scenarios the predicted increase in sediment copper concentration was small (<5 mg kg d.w.$^{-1}$) in relation to the background concentration of 21 mg kg d.w.$^{-1}$. Generally, ditches, and particularly ponds, showed greater sensitivity to inputs than streams. This reflects the nature of the predicted sediment settling in the ponds, where settling was predicted to be complete under all baseflow and soilflow conditions, with the exception of R1 pond where incomplete settling was predicted in response to soilflow events. The highest predicted risk characterisation ratio (RCR) was 0.63, in R1 pond after 50 years of application at a rate of 8 kg Cu ha^{-1} a^{-1}.

3.4 Effects of attenuation in runoff scenarios

Attenuation was observed to result in greater proportional declines in predicted surface water and sediment copper in those scenarios predicted to be relatively more sensitive to unattenuated inputs. This was because the predicted copper concentrations were not greatly elevated above the background in the relatively less sensitive scenarios, so there was less scope for reductions in predicted concentrations. For surface waters, the proportional decline in predicted copper concentrations, relative to the unattenuated scenarios, was on average 19% for 10m wide VFS and 25% for 20m wide VFS in 2030, for an input rate of 8 kg Cu ha^{-1} a^{-1}. The proportional decline in predicted concentrations due to attenuation was observed to be lower in response to a lower input rate; at 2 kg Cu ha^{-1} a^{-1}, the predicted proportional declines in 2030 were 8% for 10m wide VFS and 12% for 20m wide VFS. Predicted sediment concentrations were also reduced when attenuation was simulated. The proportional decline in predicted concentration, compared to the simulations where attenuation was not considered, was on average 10% for 10m wide VFS and 12% for 20m wide VFS in 2020, for an input rate of 8 kg Cu ha^{-1} a^{-1}. The proportional decline in predicted concentration increased with input rate: for the same year and the lowest loading rate the proportional declines were 5% and 6% respectively, for 10m wide and 20m wide VFS.

Since potential risks up to 50 years after commencement of inputs were predicted only for scenarios R1 pond and R2 stream (for surface waters only), the pattern of exceedence was only predicted to be altered by attenuation in these scenarios. No exceedence of any PNEC was seen for R2 when attenuation was simulated. Exceedences for R1 pond remained, but were generally reduced in magnitude. Attenuation did not impact the exceedence of the site-specific PNEC in 2020 in response to input rates of 6 or 8 kg Cu ha^{-1} a^{-1}. Attenuation using 20m wide, but not 10m wide, VFS limited the exceedence of the site-specific PNEC in 2030 to input rates of 6 or 8 kg Cu ha^{-1} a^{-1}. In 2060, exceedence of the reasonable worst case PNEC was limited to input rates of 6 or 8 kg Cu ha^{-1} a^{-1} when 20m VFS were simulated. Also, no exceedence of the proposed RAC was predicted in 2060 whereas in the absence of attenuation exceedence was predicted in response to input rates of 2 kg Cu ha^{-1} a^{-1} or higher.

4 Discussion

- Application of copper as a fungicide is predicted to result in gradual copper accumulation in topsoils and increases in copper concentrations in the water column and sediments of receiving waters. Accumulation over any number of years was predicted to occur at a more or less constant rate in response to a constant annual application rate. In the longer term it is reasonable to assume that accumulation in topsoil would continue in response to a continuous, constant input rate. The future rate of transfer to surface waters is less certain since there is a lack of knowledge regarding the long term ageing behaviour of copper. The aging model included in the IDMM is based on relatively short-term experiments (2 years) and predicts that aging is essentially complete after 12 months. There is currently limited evidence for the progress of aging over longer time periods. Ma et al.[7] found that two circumneutral vineyard soils from Italy, subjected to copper inputs for 80 years and having total copper concentrations of 207 and 389 mg kg $d.w.^{-1}$, had about 30% of the total copper present in labile form, a lower proportion of the total copper than was predicted by the IDMM in any soil simulated in this study. There is thus the possibility that longer term (decadal) aging may restrict copper fluxes to surface waters to a greater degree than the IDMM predicts.
- Risks due to topsoil accumulation are predicted to be driven largely by the intrinsic sensitivity of the soil to copper (i.e. the PNEC), since accumulation rates are similar for the soils simulated. Risks are predicted to be generally low for inputs commencing in 2010.
- Potential risks to soil in responses to inputs starting in 2010 are not predicted by 2020 or by 2030. Risks are predicted in seven of the scenarios by 2060.
- Risks due to increasing copper concentrations in the water column of receiving waters are predicted to vary with the intrinsic sensitivity of the waterbody, which comprises the chemical sensitivity (the PNEC) and the tendency for the waterbody to retain contaminants, which is related to its flushing time. Ponds have the longest

flushing time and are thus predicted to be more sensitive to contamination than ditches and streams.

- No risk to surface waters by 2020 or 2030 is predicted with the exception of the R1 pond scenario. Predicted risks by 2060 are confined to scenarios D2 stream, D2 ditch, R1 pond and R2 stream. Exceedence of the proposed EU RAC is seen only for R1 pond in 2060 at the three highest input rates.
- No potential risks to sediments prior to 2060 are indicated. This is in contrast to the previous simulation of copper inputs to soils[4], and results from the description of sediment behaviour implemented in the IDMM for this study. In particular, dilution of bottom sediment by settling of suspended particles from the baseflow, during periods of low soilflow, is predicted to restrict accumulation of added copper in bottom sediments.
- Simulation of attenuation in the runoff scenarios indicated that attenuation (vegetation filter strips) should cause declines in the surface water and sediment concentrations, with greater declines seen for higher loading rates. The extent to which this attenuation reduces the predicted concentrations to below the PNEC depends on the magnitude of the predicted concentrations and (for surface waters) the PNEC chosen. In the R1 pond scenario, where exceedence of PNECs in 2030 and 2060 remains extensive, RCRs are mostly between one and five when 20m wide VFS are simulated.
- Assuming that the application rates and the timescale of application simulated here are reasonable, application of copper over the next 10-50 years, in locations where application has not previously occurred, may cause some potential risks to soils, surface waters and freshwater sediments. The degree to which risk is predicted is highly dependent on the nature of the scenario, with R1 pond proving to be particularly sensitive. However, this should ideally be verified against field data for locations with well-characterised soils and known histories of copper application.
- Since copper is known to be strongly retained in soils following input (e.g. [8]) and thus to remain in soils for long periods of time following application, management of the potential risks to soils, surface waters and sediments due to copper use as a fungicide would be optimally done by considering also its bioavailability in the different compartments.

Appendix 1:Characteristics of the FOCUS scenarios

(i) general and soils

Scenario	Country	Latitude	Longitude	Mean Temperature (°C)	Bulk density g cm^{-3}	pH_{ss}	%OM	%clay	Texture	Crops simulated
D1	Sweden	58.33	13.05	6.1	1.35	7.7	4.0	47	Silty clay	Apples
D2	UK	51.65	-1.63	9.7	1.25	7.7	4.8	55	Clay	Apples
D3	Netherlands	51.53	5.87	9.9	1.35	6.0	4.6	3	Sand	Apples
D4	Denmark	55.62	12.08	8.2	1.51	7.4	2.6	12	Loam	Apples
D5	France	47.45	0.97	11.8	1.56	7.1	3.8	20	Loam	Apples
D6	Greece	38.38	23.10	16.7	1.35	7.9	2.4	30	Clay loam	Grapes, olives, oranges
R1	Germany	49.00	8.67	10.0	1.43	7.8	2.4	13	Silt loam	Apples, grapes, hops
R2	Portugal	41.18	-8.07	14.8	1.20	5.4	6.8	13	Sandy loam	Apples, grapes
R3	Italy	44.50	11.40	13.6	1.46	8.3	2.0	34	Clay loam	Apples, grapes
R4	France	43.50	3.32	14.0	1.52	8.7	1.2	25	Sandy clay loam	Apples, grapes, olives, oranges

(ii) surface waters

Scenario	Country	pH	DOC mg l^{-1} [a]	Σ (Na, Mg, K, Ca) μeq l^{-1} [b]	Ditch baseflow mm a^{-1}	Stream baseflow mm a^{-1}	Pond baseflow mm a^{-1}
D1	Sweden	6.4	14.6	0.55	8.4	12.0	
D2	UK	8.3	3.6	6.86	1.1	0.2	
D3	Netherlands	7.4	10.1	4.31	84.2		
D4	Denmark	7.6	19.0	4.15		38.8	0.3
D5	France	8.0	2.8	6.38		27.1	0.3
D6	Greece	8.1	0.8	5.53	42.1		
R1	Germany	7.9	1.6	4.37		70.1	1.1
R2	Portugal	6.5	2.4	0.95		102.2	
R3	Italy	8.3	1.7	6.74		27.8	
R4	France	8.1	1.6	1.43		70.4	

[a] dissolved organic carbon.

[b] sum of the concentrations of the major cations sodium, magnesium, potassium and calcium.

Appendix 2: Computation of copper removal in harvestable plant material

Plant yields

The plants to be simulated for each scenario are given in the table below.

Scenario	Country	Crop				
		Apples	Grapes	Oranges	Hops	Olives
D1	Sweden	✓	–	–	–	–
D2	UK	✓	–	–	–	–
D3	Netherlands	✓	–	–	–	–
D4	Denmark	✓	–	–	–	–
D5	France	✓	–	–	–	–
D6	Greece	–	✓	✓	–	✓
R1	Germany	✓	✓	–	✓	–
R2	Portugal	✓	✓	–	–	–
R3	Italy	✓	✓	–	–	–
R4	France	✓	✓	✓	–	✓

Available data on yields of the harvestable parts of plants in the relevant countries were obtained from the Food and Agriculture Organisation of the United Nations statistical database (FAOSTAT[9]). Starting years for which yield data were available are listed below (all records are up to 2009):

Scenario	Country	Plant				
		Apples	Grapes	Oranges	Hops	Olives
D1	Sweden	1985	–	–	–	–
D2	UK	1961	–	–	–	–
D3	Netherlands	1984	–	–	–	–
D4	Denmark	1985	–	–	–	–
D5	France	1961	–	–	–	–
D6	Greece	–	1961	1961	–	1985
R1	Germany	1985	1961	–	1961	–
R2	Portugal	1961	1961	–	–	–
R3	Italy	1961	1961	–	–	–
R4	France	1961	1961	1961	–	1961

Time trends of plant yields were calculated as follows:

1. Period covered by FAO yield data (1961-2009 or 1985-2009). Either a linear trend in yield over time, or no trend, was assumed. If a significant increase or decrease in yield occurred during the period, a linear trend was used, which was found to adequately describe the trend in all cases. Where no trend was apparent the mean yield value for the period was used.
2. Period from 1700 to 1961 or 1985. The trend in yield was assumed to follow that of European per capita Gross Domestic Product (GDP), such that

$$\mathbf{Yld_{yr}} = \mathbf{Yld_{p\_yr}} \cdot \frac{\mathbf{GDP_{yr}}}{\mathbf{GDP_{p\_yr}}}$$

where Yld is the yield (tons fresh weight ha^{-1}), GDP is the known GDP and the subscripts $_{yr}$ and $_{p\_yr}$ refer to the year for which the yield is being calculated and the first year for which FAO data are available. The time trend in per capita GDP was taken from [10].

Copper content of harvestable parts of plants

Copper contents of the harvestable parts of plants, with the exception of hops, were taken from the USDA National Nutrient Database for Standard Reference[11]. The copper content of hops was taken from Vinas et al, 2002[12]. The copper contents used are given in the table below:

Crop	Copper content g (ton fresh weight)$^{-1}$
Apples	0.29
Grapes	1.27
Oranges	0.57
Hops	2.04[a]
Olives	2.51

[a] Calculated from a copper content of 13.6 g (ton fresh weight)$^{-1}$, assuming a water content of 85% by weight.

Annual copper removal in the harvestable parts of plants

Annual copper removal (g ha^{-1} a^{-1}) is simply calculated as the copper concentration in the plant harvest (g (ton fresh weight)$^{-1}$) multiplied by the plant yield (tons fresh weight ha^{-1} a^{-1}).

Appendix 3: Predicted No Effect Concentrations (PNECs) for copper in topsoils, surface waters and sediments

Scenario	PNECs		
	Soil	Water	Sediment
	µg g^{-1}	µg l^{-1}	µg g^{-1}
D1	139	30.1	87
D2	157	1.9	87
D3	55	17.4	87
D4	67	47.0	87
D5	97	4.1	87
D6	94	1.3	87
R1	64	3.0	87
R2	98	4.0	87
R3	90	2.4	87
R4	62	4.1	87

Appendix 4: Tables of predicted copper concentration in topsoils, surface waters and sediments, and Risk Characterisation Ratios (RCRs), in the absence of runoff attenuation

Predicted concentrations and RCRs are presented for the present day and for the years 2020, 2030 and 2060. Units of predicted concentrations are µg g^{-1} for soils, µg l^{-1} for waters and µg g^{-1} for sediments. The RCR values are listed below the predicted concentrations. Values greater than or equal to one, indicating a potential risk, are highlighted in bold.

Table A4-1. Predicted copper concentrations and RCRs for scenario D1.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
soil				
present day	9.8 0.18	9.8 0.18	9.8 0.18	9.8 0.18
2020	10.3 0.07	10.8 0.08	11.3 0.08	11.8 0.08
2030	15.2 0.11	20.7 0.15	26.1 0.19	31.5 0.23
2060	35.0 0.25	60.2 0.43	85.3 0.61	110.5 0.79
water - stream				
present day	0.9 0.03	0.9 0.03	0.9 0.03	0.9 0.03
2020	1.0 0.03	1.0 0.03	1.1 0.04	1.2 0.04
2030	1.0 0.03	1.2 0.04	1.3 0.04	1.4 0.05
2060	1.2 0.04	1.6 0.05	1.9 0.06	2.2 0.07
water – ditch				
present day	0.9 0.03	0.9 0.03	0.9 0.03	0.9 0.03
2020	1.0 0.03	1.1 0.04	1.1 0.04	1.2 0.04
2030	1.1 0.04	1.2 0.04	1.4 0.05	1.5 0.05
2060	1.3 0.04	1.7 0.06	2.1 0.07	2.5 0.08
sediment – stream				
present day	20.9 0.24	20.9 0.24	20.9 0.24	20.9 0.24
2020	20.9 0.23	21.0 0.24	21.1 0.24	21.5 0.25
2030	21.1 0.24	21.3 0.25	21.5 0.25	22.1 0.25
2060	22.4 0.26	23.0 0.26	23.9 0.27	25.3 0.29
sediment – ditch				
present day	21.8 0.25	21.8 0.25	21.8 0.25	21.8 0.25
2020	22.0 0.25	22.1 0.25	22.3 0.26	22.4 0.26
2030	22.4 0.26	22.9 0.26	23.4 0.27	23.9 0.27
2060	24.0 0.29	27.6 0.32	30.2 0.35	32.9 0.38

Table A4-2. Predicted copper concentrations and RCRs for scenario D2.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
soil				
present day	25.4 0.17	25.4 0.17	25.4 0.17	25.4 0.17
2020	31.4 0.20	37.2 0.24	43.1 0.27	49.0 0.31
2030	36.8 0.23	48.0 0.31	59.2 0.38	70.4 0.45
2060	53.1 0.34	80.2 0.51	107.4 0.68	134.5 0.86
water - stream				
present day	1.0 0.52	1.0 0.52	1.0 0.52	1.0 0.52
2020	1.1 0.55	1.1 0.58	1.2 0.61	1.2 0.64
2030	1.1 0.59	1.2 0.65	1.3 0.71	1.5 0.77
2060	1.3 0.69	1.6 0.85	1.9 **1.01**	2.2 **1.17**
water - ditch				
present day	1.0 0.54	1.0 0.54	1.0 0.54	1.0 0.54
2020	1.1 0.59	1.2 0.62	1.3 0.66	1.3 0.70
2030	1.2 0.63	1.3 0.71	1.5 0.79	1.7 0.88
2060	1.5 0.77	1.9 0.98	2.3 **1.19**	2.7 **1.40**
sediment - stream				
present day	23.2 0.27	23.2 0.27	23.2 0.27	23.2 0.27
2020	23.3 0.27	23.6 0.27	23.7 0.27	23.8 0.27
2030	23.8 0.27	24.4 0.28	24.7 0.28	25.0 0.29
2060	26.0 0.30	28.1 0.32	29.8 0.34	31.5 0.36
sediment - ditch				
present day	28.3 0.32	28.3 0.32	28.3 0.32	28.3 0.32
2020	28.8 0.33	29.8 0.34	30.1 0.35	30.3 0.35
2030	30.5 0.35	32.3 0.37	33.3 0.38	34.3 0.39
2060	37.7 0.43	44.5 0.51	50.1 0.58	55.6 0.64

Table A4-3. Predicted copper concentrations and RCRs for scenario D3.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
soil				
present day	11.3	11.3	11.3	11.3
	0.21	0.21	0.21	0.21
2020	16.7	22.1	27.5	32.9
	0.30	0.40	0.50	0.60
2030	21.6	31.9	42.3	52.6
	0.39	0.58	0.88	0.96
2060	36.3	61.3	86.4	111.5
	0.66	**1.12**	**1.57**	**2.03**
water - ditch				
present day	0.9	0.9	0.9	0.9
	0.05	0.05	0.05	0.05
2020	1.1	1.2	1.4	1.5
	0.06	0.07	0.08	0.09
2030	1.2	1.5	1.8	2.1
	0.07	0.09	0.10	0.12
2060	1.6	2.3	3.0	3.7
	0.09	0.13	0.17	0.21
sediment - ditch				
present day	22.9	22.9	22.9	22.9
	0.26	0.26	0.26	0.26
2020	23.5	23.7	24.0	24.2
	0.27	0.27	0.28	0.28
2030	24.5	25.5	26.6	27.6
	0.28	0.29	0.31	0.32
2060	29.9	35.8	41.7	47.6
	0.34	0.41	0.48	0.55

Table A4-4. Predicted copper concentrations and RCRs for scenario D4.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
Soil				
present day	6.2 0.09	6.2 0.09	6.2 0.09	6.2 0.09
2020	11.1 0.17	15.9 0.24	20.8 0.31	25.6 0.38
2030	15.5 0.23	24.7 0.37	34.0 0.51	43.3 0.65
2060	28.7 0.43	51.2 0.76	73.6 **1.10**	96.1 **1.43**
water - stream				
present day	0.9 0.02	0.9 0.02	0.9 0.02	0.9 0.02
2020	1.0 0.02	1.0 0.02	1.1 0.02	1.2 0.02
2030	1.0 0.02	1.2 0.02	1.3 0.03	1.4 0.03
2060	1.2 0.03	1.6 0.03	1.9 0.04	2.3 0.05
water - pond				
present day	0.9 0.02	0.9 0.02	0.9 0.02	0.9 0.02
2020	1.4 0.03	1.3 0.03	1.4 0.03	1.6 0.03
2030	1.6 0.03	1.6 0.03	1.9 0.04	2.1 0.05
2060	2.0 0.04	2.5 0.05	3.2 0.07	3.9 0.08
sediment - stream				
present day	21.1 0.24	21.1 0.24	21.1 0.24	21.1 0.24
2020	21.1 0.24	21.2 0.24	21.2 0.24	21.2 0.24
2030	21.2 0.24	21.3 0.25	21.4 0.25	21.6 0.25
2060	21.7 0.25	22.3 0.26	22.9 0.26	23.6 0.27
sediment – pond				
present day	21.2 0.24	21.2 0.24	21.2 0.24	21.2 0.24
2020	21.3 0.25	21.3 0.24	21.4 0.25	21.4 0.25
2030	21.5 0.25	21.7 0.25	21.9 0.25	22.1 0.25
2060	22.6 0.26	23.8 0.27	24.9 0.29	26.1 0.30

Table A4-5. Predicted copper concentrations and RCRs for scenario D5.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
soil				
present day	9.6 0.10	9.6 0.10	9.6 0.10	9.6 0.10
2020	14.2 0.15	18.9 0.20	23.6 0.24	28.3 0.29
2030	18.5 0.19	27.4 0.28	36.4 0.38	45.4 0.47
2060	31.2 0.32	52.9 0.55	74.7 0.77	96.4 0.99
water - stream				
present day	0.9 0.21	0.9 0.21	0.9 0.21	0.9 0.21
2020	0.9 0.22	0.9 0.23	1.0 0.24	1.0 0.24
2030	0.9 0.23	1.0 0.24	1.1 0.26	1.1 0.28
2060	1.0 0.25	1.2 0.30	1.4 0.34	1.6 0.38
water - pond				
present day	0.9 0.21	0.9 0.21	0.9 0.21	0.9 0.21
2020	0.9 0.22	0.9 0.22	1.0 0.23	1.0 0.24
2030	0.9 0.22	1.0 0.24	1.1 0.26	1.1 0.28
2060	1.0 0.25	1.2 0.30	1.4 0.34	1.6 0.39
sediment - stream				
present day	20.9 0.24	20.9 0.24	20.9 0.24	20.9 0.24
2020	20.9 0.24	21.0 0.24	21.0 0.24	21.0 0.24
2030	21.0 0.24	21.1 0.24	21.2 0.24	21.2 0.24
2060	21.4 0.25	21.8 0.25	22.3 0.26	22.7 0.26
sediment – pond				
present day	20.8 0.24	20.8 0.24	20.8 0.24	20.8 0.24
2020	20.9 0.24	21.0 0.24	21.1 0.24	21.2 0.24
2030	21.2 0.24	21.6 0.25	22.0 0.25	22.5 0.26
2060	23.1 0.27	25.5 0.29	27.9 0.32	30.3 0.35

Table A4-6. Predicted copper concentrations and RCRs for scenario D6.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
soil				
present day	24.7 0.27	24.7 0.27	24.7 0.27	24.7 0.27
2020	29.8 0.32	34.9 0.37	40.1 0.43	45.2 0.48
2030	34.4 0.37	44.2 0.47	54.0 0.57	63.8 0.68
2060	48.3 0.51	72.0 0.77	95.7 **1.02**	119.4 **1.27**
water - ditch				
present day	0.8 0.65	0.8 0.65	0.8 0.65	0.8 0.65
2020	0.9 0.66	0.9 0.67	0.9 0.69	0.9 0.70
2030	0.9 0.68	0.9 0.70	0.9 0.73	1.0 0.75
2060	0.9 0.72	1.0 0.78	1.1 0.85	1.2 0.93
sediment – ditch				
present day	21.1 0.24	21.1 0.24	21.1 0.24	21.1 0.24
2020	21.4 0.24	21.4 0.25	21.6 0.25	21.7 0.25
2030	21.7 0.25	22.4 0.26	23.1 0.27	23.6 0.27
2060	24.0 0.28	28.4 0.33	32.0 0.37	35.4 0.41

Table A4-7. Predicted copper concentrations and RCRs for scenario R1.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
Soil				
present day	15.0 0.23	15.0 0.23	15.0 0.23	15.0 0.23
2020	20.4 0.32	25.9 0.40	31.3 0.49	36.7 0.57
2030	25.3 0.40	35.7 0.56	46.0 0.72	56.3 0.88
2060	39.9 0.62	64.9 **1.01**	89.8 **1.40**	114.8 **1.79**
water - stream				
present day	0.9 0.29	0.9 0.29	0.9 0.29	0.9 0.29
2020	0.9 0.31	1.0 0.34	1.1 0.35	1.1 0.37
2030	1.0 0.33	1.1 0.37	1.2 0.41	1.3 0.44
2060	1.2 0.39	1.4 0.47	1.6 0.55	1.9 0.62
water - pond				
present day	1.4 0.46	1.4 0.46	1.4 0.46	1.4 0.46
2020	2.5 0.85	3.5 **1.18**	4.5 **1.50**	5.5 **1.82**
2030	3.6 **1.19**	5.5 **1.84**	7.4 **2.47**	9.3 **3.10**
2060	6.5 **2.16**	11.2 **3.73**	15.9 **5.30**	20.7 **6.89**
sediment - stream				
present day	21.6 0.25	21.6 0.25	21.6 0.25	21.6 0.25
2020	21.6 0.25	21.9 0.25	22.0 0.25	22.1 0.25
2030	22.0 0.25	22.6 0.26	23.0 0.26	23.3 0.27
2060	24.1 0.28	26.5 0.30	28.6 0.33	30.7 0.35
sediment - pond				
present day	23.3 0.27	23.3 0.27	23.3 0.27	23.3 0.27
2020	23.5 0.27	24.4 0.28	24.7 0.28	25.1 0.29
2030	24.9 0.29	26.8 0.31	28.2 0.32	29.5 0.34
2060	32.3 0.37	40.5 0.47	47.7 0.55	54.7 0.63

Table A4-8. Predicted copper concentrations and RCRs for scenario R2.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
soil				
present day	8.3 0.08	8.3 0.08	8.3 0.08	8.3 0.08
2020	14.3 0.15	20.4 0.21	26.5 0.27	32.5 0.33
2030	19.7 0.20	31.3 0.32	42.8 0.44	54.3 0.55
2060	35.8 0.37	63.5 0.65	91.1 0.93	118.8 **1.21**
water - stream				
present day	0.9 0.21	0.9 0.21	0.9 0.21	0.9 0.21
2020	1.1 0.28	1.4 0.35	1.6 0.40	1.8 0.46
2030	1.4 0.34	1.8 0.46	2.3 0.58	2.8 0.69
2060	2.0 0.51	3.2 0.79	4.3 **1.09**	5.6 **1.39**
sediment - stream				
present day	21.2 0.24	21.2 0.24	21.2 0.24	21.2 0.24
2020	21.3 0.24	21.4 0.25	21.6 0.25	21.7 0.25
2030	21.7 0.25	22.2 0.25	22.6 0.26	23.1 0.27
2060	24.0 0.28	26.5 0.30	29.0 0.33	31.4 0.36

Table A4-9. Predicted copper concentrations and RCRs for scenario R3.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
soil				
present day	30.9 0.34	30.9 0.34	30.9 0.34	30.9 0.34
2020	35.9 0.40	40.9 0.45	45.9 0.51	50.9 0.57
2030	40.4 0.45	49.9 0.55	59.4 0.66	68.9 0.77
2060	53.9 0.60	76.8 0.85	99.7 **1.11**	122.6 **1.36**
water - stream				
present day	0.9 0.37	0.9 0.37	0.9 0.37	0.9 0.37
2020	0.9 0.38	0.9 0.39	1.0 0.40	1.0 0.41
2030	0.9 0.39	1.0 0.41	1.0 0.42	1.1 0.44
2060	1.0 0.41	1.1 0.45	1.2 0.49	1.3 0.53
sediment - stream				
present day	24.5 0.28	24.5 0.28	24.5 0.28	24.5 0.28
2020	25.1 0.29	25.2 0.29	25.3 0.29	25.4 0.29
2030	25.9 0.30	26.4 0.30	26.9 0.31	27.3 0.31
2060	29.3 0.34	32.2 0.37	35.0 0.40	37.7 0.43

Table A4-10. Predicted copper concentrations and RCRs for scenario R4.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
soil				
present day	19.8	19.8	19.8	19.8
	0.32	0.32	0.32	0.32
2020	25	29	34	39
	0.40	0.47	0.55	0.63
2030	29	38	47	57
	0.47	0.61	0.76	0.91
2060	42	64	86	109
	0.68	**1.04**	**1.39**	**1.75**
water - stream				
present day	0.8	0.8	0.8	0.8
	0.20	0.20	0.20	0.20
2020	0.8	0.9	0.9	0.9
	0.21	0.21	0.21	0.21
2030	0.9	0.9	0.9	0.9
	0.21	0.21	0.22	0.22
2060	0.9	0.9	1.0	1.0
	0.21	0.22	0.23	0.24
sediment - stream				
present day	20.9	20.9	20.9	20.9
	0.24	0.24	0.24	0.24
2020	20.9	20.9	21.0	21.1
	0.24	0.24	0.24	0.24
2030	21.0	21.2	21.3	21.6
	0.24	0.24	0.25	0.25
2060	21.8	22.7	23.6	24.6
	0.25	0.26	0.27	0.28

Appendix 5: Tables of predicted copper concentration in topsoils, surface waters and sediments, and Risk Characterisation Ratios (RCRs), with attenuation due to 10m wide vegetation filter strips (runoff scenarios only)

Predicted concentrations and RCRs are presented for the years 2020, 2030 and 2060. Units of predicted concentrations are µg g^{-1} for soils, µg l^{-1} for waters and µg g^{-1} for sediments. The RCR values are listed below the predicted concentrations. Values greater than or equal to one, indicating a potential risk, are highlighted in bold.

Table A5-1. Predicted copper concentrations and RCRs in waters for scenario R1, simulating VFS of 10m width.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
water - stream				
2020	0.9 0.30	0.9 0.31	1.0 0.32	1.0 0.33
2030	0.9 0.31	1.0 0.3	1.0 0.34	1.1 0.36
2060	1.0 0.34	1.1 0.37	1.2 0.41	1.3 0.44
water - pond				
2020	2.3 0.76	3.0 0.99	3.5 **1.18**	4.1 **1.36**
2030	3.0 **1.00**	4.2 **1.40**	5.2 **1.74**	6.2 **2.06**
2060	4.8 **1.60**	7.3 **2.43**	9.5 **3.18**	11.7 **3.91**
sediment – stream				
2020	21.5 0.25	21.5 0.25	21.5 0.25	21.6 0.25
2030	21.7 0.25	21.8 0.25	21.9 0.25	22.1 0.25
2060	22.6 0.26	23.4 0.27	24.2 0.28	25.0 0.29
sediment - pond				
2020	21.5 0.25	21.6 0.25	21.6 0.25	21.7 0.25
2030	21.7 0.25	21.9 0.25	22.2 0.25	22.4 0.26
2060	22.9 0.26	24.1 0.28	25.2 0.29	26.3 0.30

Table A5-2. Predicted copper concentrations and RCRs for scenario R2, simulating VFS of 10m width.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
water - stream				
2020	1.0 0.26	1.2 0.30	1.3 0.33	1.5 0.36
2030	1.2 0.30	1.5 0.36	1.7 0.42	1.9 0.48
2060	1.6 0.39	2.2 0.54	2.7 0.68	3.3 0.82
sediment - stream				
2020	21.2 0.24	21.2 0.24	21.3 0.24	21.3 0.24
2030	21.3 0.25	21.5 0.25	21.7 0.25	21.9 0.25
2060	22.3 0.26	23.3 0.27	24.2 0.28	25.1 0.29

Table A5-3. Predicted copper concentrations and RCRs for scenario R3, simulating VFS of 10m width.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
water - stream				
2020	0.9 0.37	0.9 0.37	0.9 0.38	0.9 0.38
2030	0.9 0.37	0.9 0.38	0.9 0.39	0.9 0.39
2060	0.9 0.38	1.0 0.40	1.0 0.42	1.0 0.44
sediment - stream				
2020	22.8 0.26	22.8 0.26	22.9 0.26	22.9 0.26
2030	23.1 0.27	23.3 0.27	23.5 0.27	23.6 0.27
2060	24.4 0.28	25.5 0.29	26.5 0.30	27.5 0.32

Table A5-4. Predicted copper concentrations and RCRs for scenario R4, simulating VFS of 10m width.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
water – stream				
2020	0.8 0.21	0.9 0.21	0.9 0.21	0.9 0.21
2030	0.9 0.21	0.9 0.21	0.9 0.21	0.9 0.21
2060	0.9 0.21	0.9 0.21	0.9 0.22	0.9 0.22
sediment - stream				
2020	20.9 0.24	21.0 0.24	21.0 0.24	21.0 0.24
2030	21.0 0.24	21.1 0.24	21.1 0.24	21.2 0.24
2060	21.3 0.24	21.6 0.25	22.0 0.25	22.3 0.26

Appendix 6: Tables of predicted copper concentration in topsoils, surface waters and sediments, and Risk Characterisation Ratios (RCRs), with attenuation due to 20m wide vegetation filter strips (runoff scenarios only)

Predicted concentrations and RCRs are presented for the years 2020, 2030 and 2060. Units of predicted concentrations are µg g^{-1} for soils, µg l^{-1} for waters and µg g^{-1} for sediments. The RCR values are listed below the predicted concentrations. Values greater than or equal to one, indicating a potential risk, are highlighted in bold.

Table A6-1. Predicted copper concentrations and RCRs in waters for scenario R1, simulating VFS of 20m width.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
water - stream				
2020	0.9 0.30	0.9 0.30	0.9 0.31	0.9 0.31
2030	0.9 0.30	0.9 0.31	1.0 0.32	1.0 0.32
2060	1.0 0.32	1.0 0.34	1.1 0.36	1.1 0.38
water – pond				
2020	2.1 0.71	2.7 0.89	3.2 **1.05**	3.6 **1.20**
2030	2.7 0.91	3.7 **1.23**	4.5 **1.49**	5.2 **1.74**
2060	4.2 **1.41**	6.1 **2.03**	7.7 **2.58**	9.3 **3.10**
sediment – stream				
2020	21.4 0.25	21.4 0.25	21.4 0.25	21.4 0.25
2030	21.5 0.25	21.6 0.25	21.7 0.25	21.8 0.25
2060	22.2 0.25	22.7 0.26	23.2 0.27	23.7 0.27
sediment – pond				
2020	21.2 0.24	21.2 0.24	21.2 0.24	21.2 0.24
2030	21.3 0.24	21.3 0.25	21.4 0.25	21.5 0.25
2060	21.7 0.25	22.1 0.25	22.5 0.26	22.9 0.26

Table A6-2. Predicted copper concentrations and RCRs for scenario R2, simulating VFS of 20m width.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
water - stream				
2020	1.0 0.25	1.1 0.28	1.2 0.30	1.3 0.32
2030	1.1 0.28	1.3 0.32	1.4 0.36	1.6 0.40
2060	1.4 0.34	1.8 0.44	2.1 0.53	2.5 0.62
sediment – stream				
2020	21.1 0.24	21.2 0.24	21.2 0.24	21.2 0.24
2030	21.2 0.24	21.4 0.25	21.5 0.25	21.6 0.25
2060	21.9 0.25	22.6 0.26	23.3 0.27	23.9 0.27

Table A6-3. Predicted copper concentrations and RCRs for scenario R3, simulating VFS of 20m width.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
water - stream				
2020	0.9 0.36	0.9 0.37	0.9 0.37	0.9 0.37
2030	0.9 0.37	0.9 0.37	0.9 0.38	0.9 0.38
2060	0.9 0.37	0.9 0.39	1.0 0.40	1.0 0.41
sediment - stream				
2020	22.2 0.26	22.3 0.26	22.3 0.26	22.3 0.26
2030	22.4 0.26	22.6 0.26	22.7 0.26	22.8 0.26
2060	23.3 0.27	24.0 0.28	24.6 0.28	25.2 0.29

Table A6-4. Predicted copper concentrations and RCRs for scenario R4, simulating VFS of 20m width.

	Copper application rate kg ha^{-1} a^{-1}			
	2	4	6	8
water – stream				
2020	0.8 0.21	0.8 0.21	0.9 0.21	0.9 0.21
2030	0.8 0.21	0.9 0.21	0.9 0.21	0.9 0.21
2060	0.9 0.21	0.9 0.21	0.9 0.22	0.9 0.22
sediment - stream				
2020	20.9 0.24	21.0 0.24	21.0 0.24	21.0 0.24
2030	21.0 0.24	21.0 0.24	21.1 0.24	21.1 0.24
2060	21.4 0.24	21.4 0.25	21.7 0.25	21.9 0.25

Appendix 7: Charts of copper concentrations in topsoils, surface waters and sediments, in the absence of vegetation filter strips

Charts show the evolution of predicted copper concentrations from 2000 (representing pre-contamination conditions) to 2060. Concentrations resulting from specific application rates are denoted as follows on the charts:

2 kg Cu ha^{-1} a^{-1}	Solid green line
4 kg Cu ha^{-1} a^{-1}	Dashed yellow line
6 kg Cu ha^{-1} a^{-1}	Dash-dot orange line
8 kg Cu ha^{-1} a^{-1}	Dash-dot-dot red line

On each chart, the relevant copper PNEC is indicated by a solid horizontal blue line. On the chart displaying the simulations of surface water concentrations, the ‘reasonable’ worst case’ PNEC of 6.8 µg l^{-1} copper is displayed as a dashed horizontal blue line, and the proposed EU RAC of 9.5 µg l^{-1} is displayed as a thick red line.

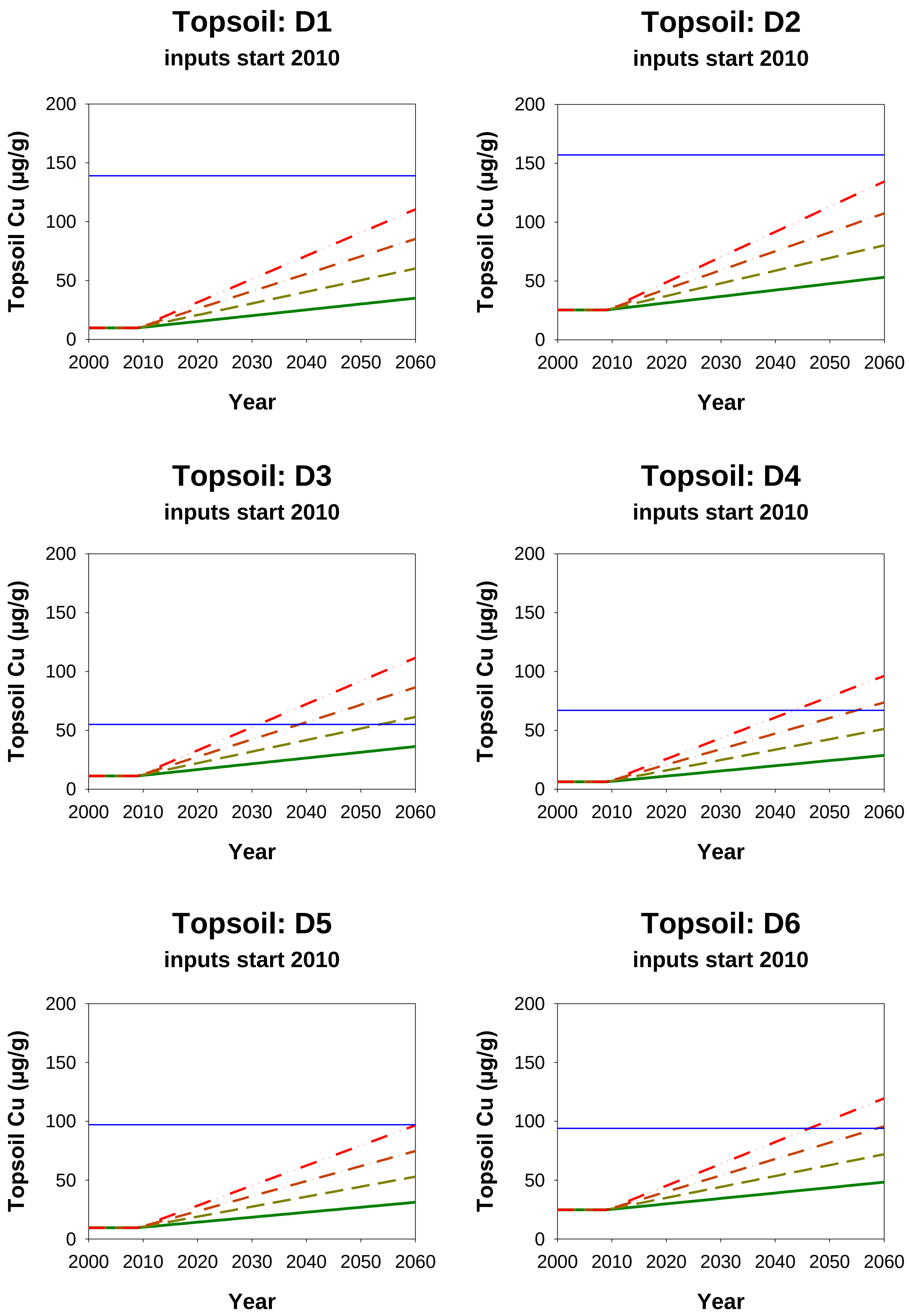


Figure A7-1. Topsoil copper accumulation for scenarios D1 to D6.

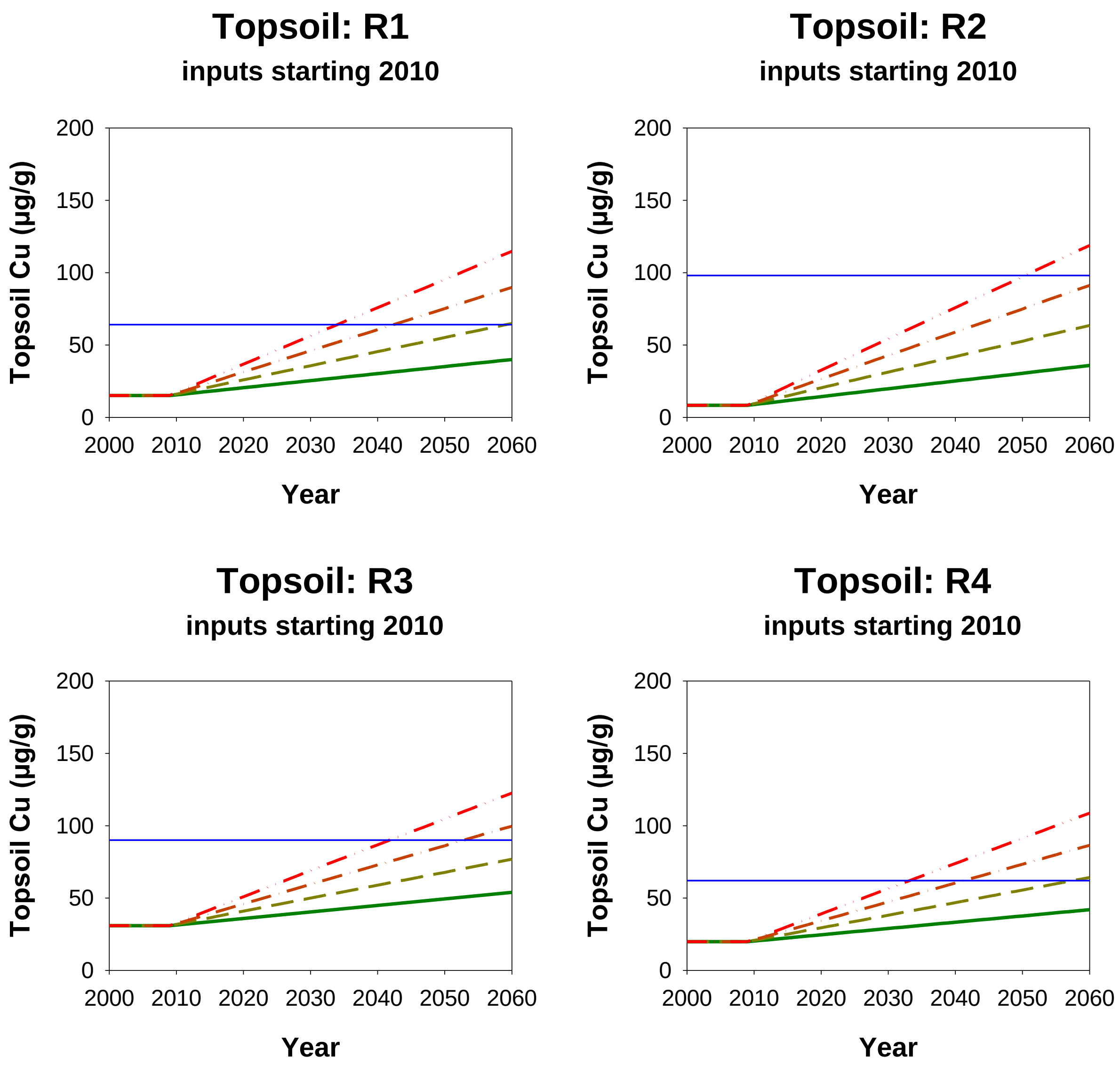


Figure A7-2. Topsoil copper accumulation for scenarios R1 to R4.

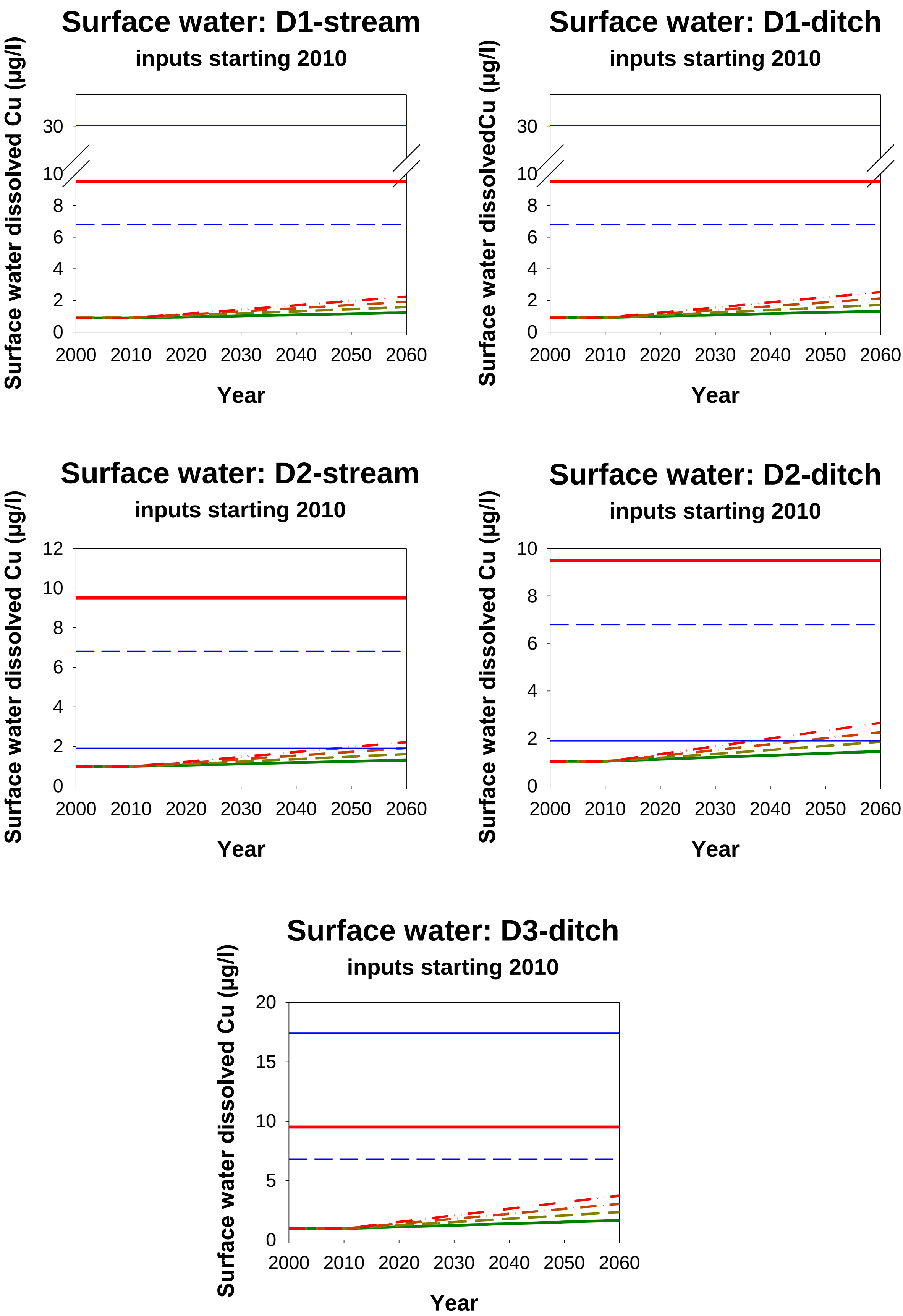


Figure A7-3. Copper surface water concentrations for scenarios D1-D3.

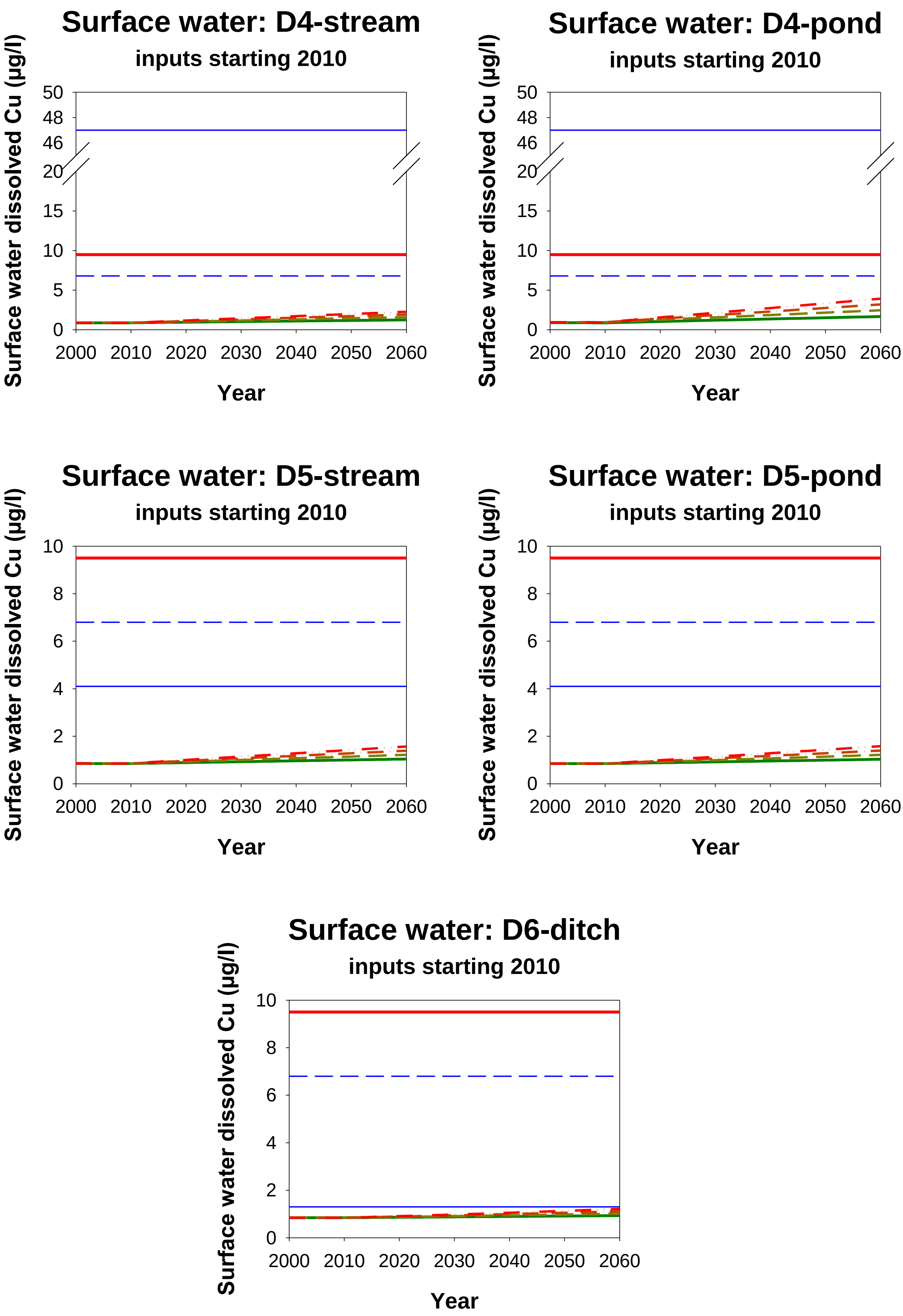


Figure A7-4. Copper surface water concentrations for scenarios D4-D6.

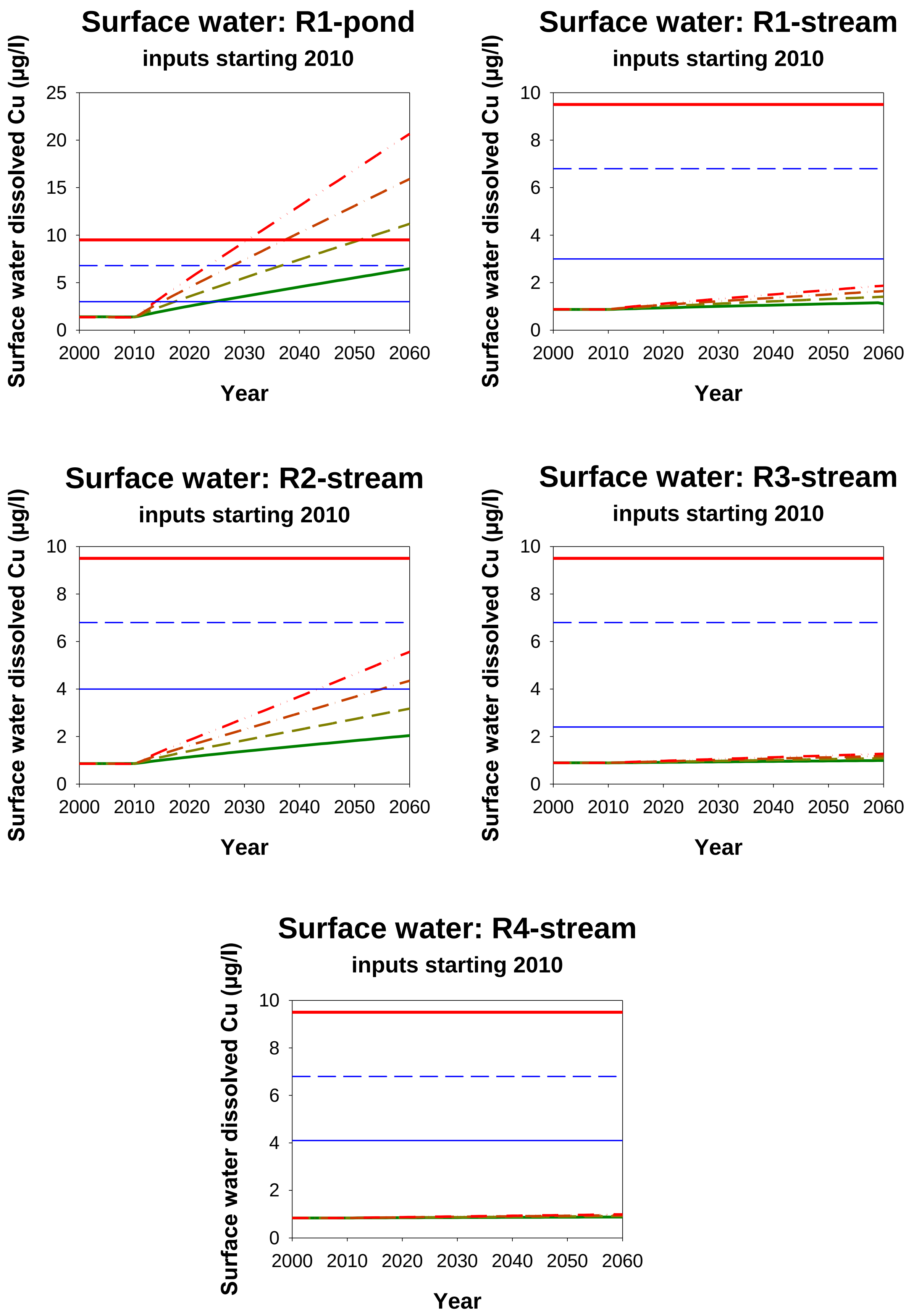


Figure A7-5. Copper surface water concentrations for scenarios R1-R4.

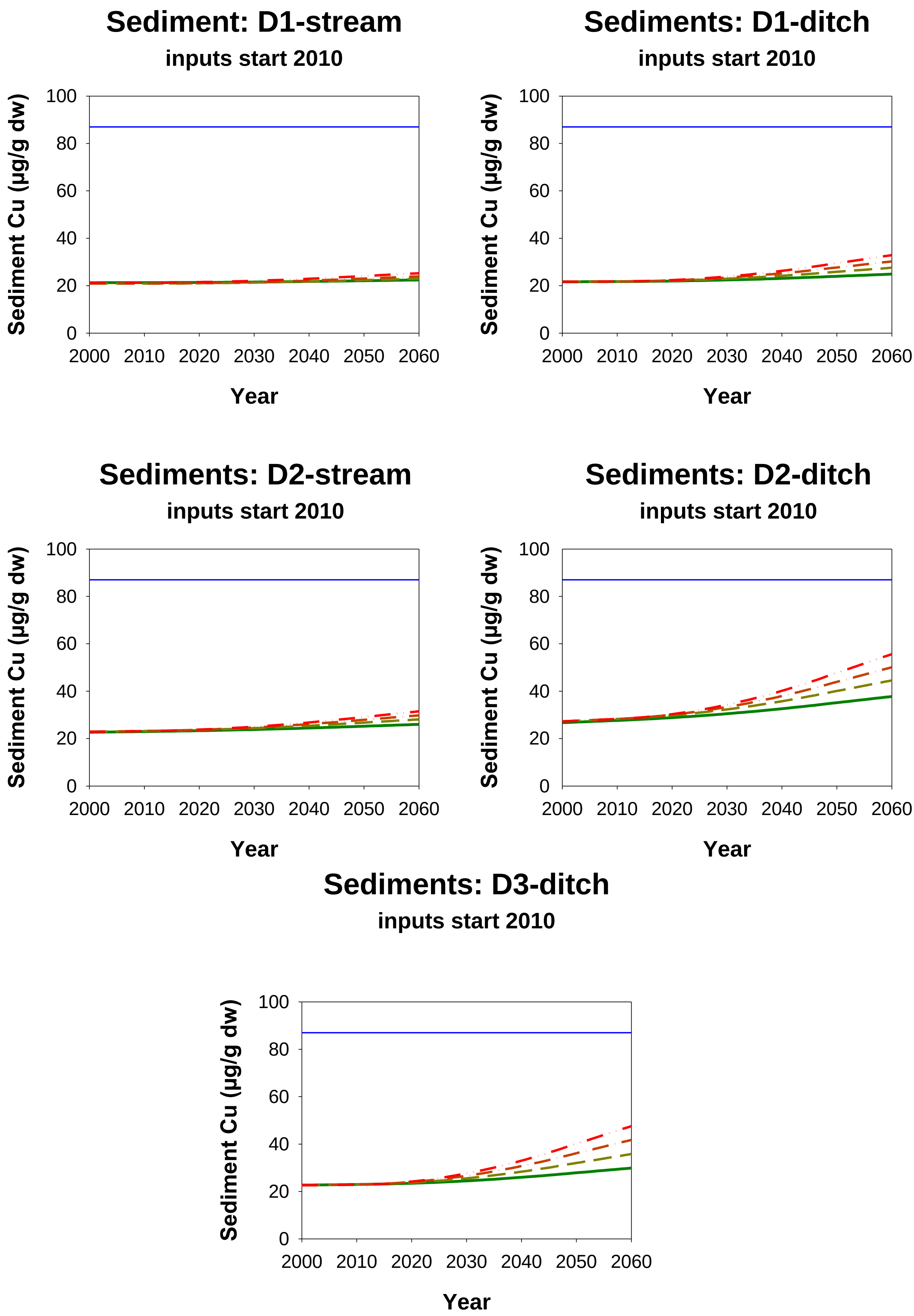


Figure A7-6. Copper sediment concentrations for scenarios D1-D3.

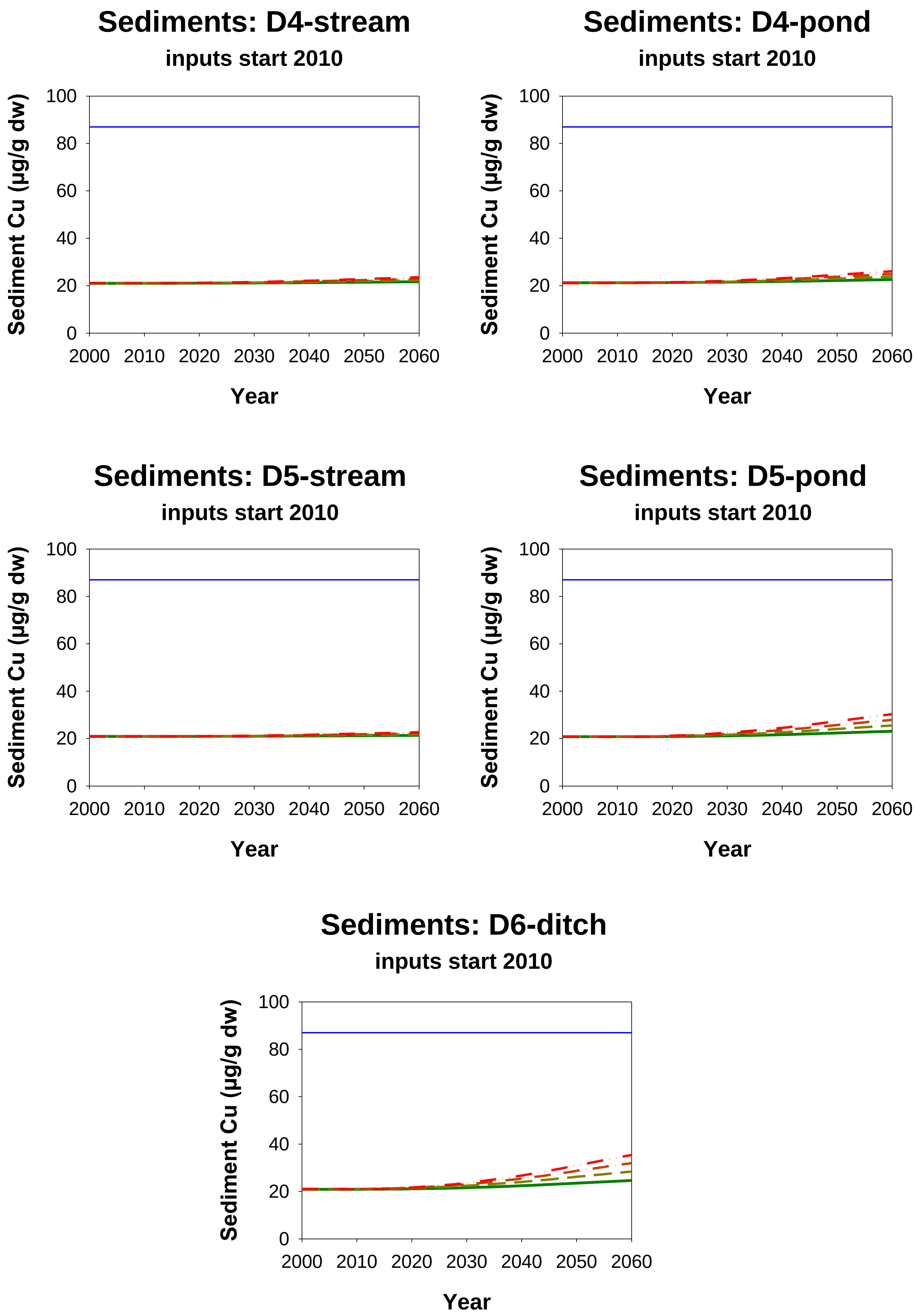


Figure A7-7. Copper sediment concentrations for scenarios D4-D6.

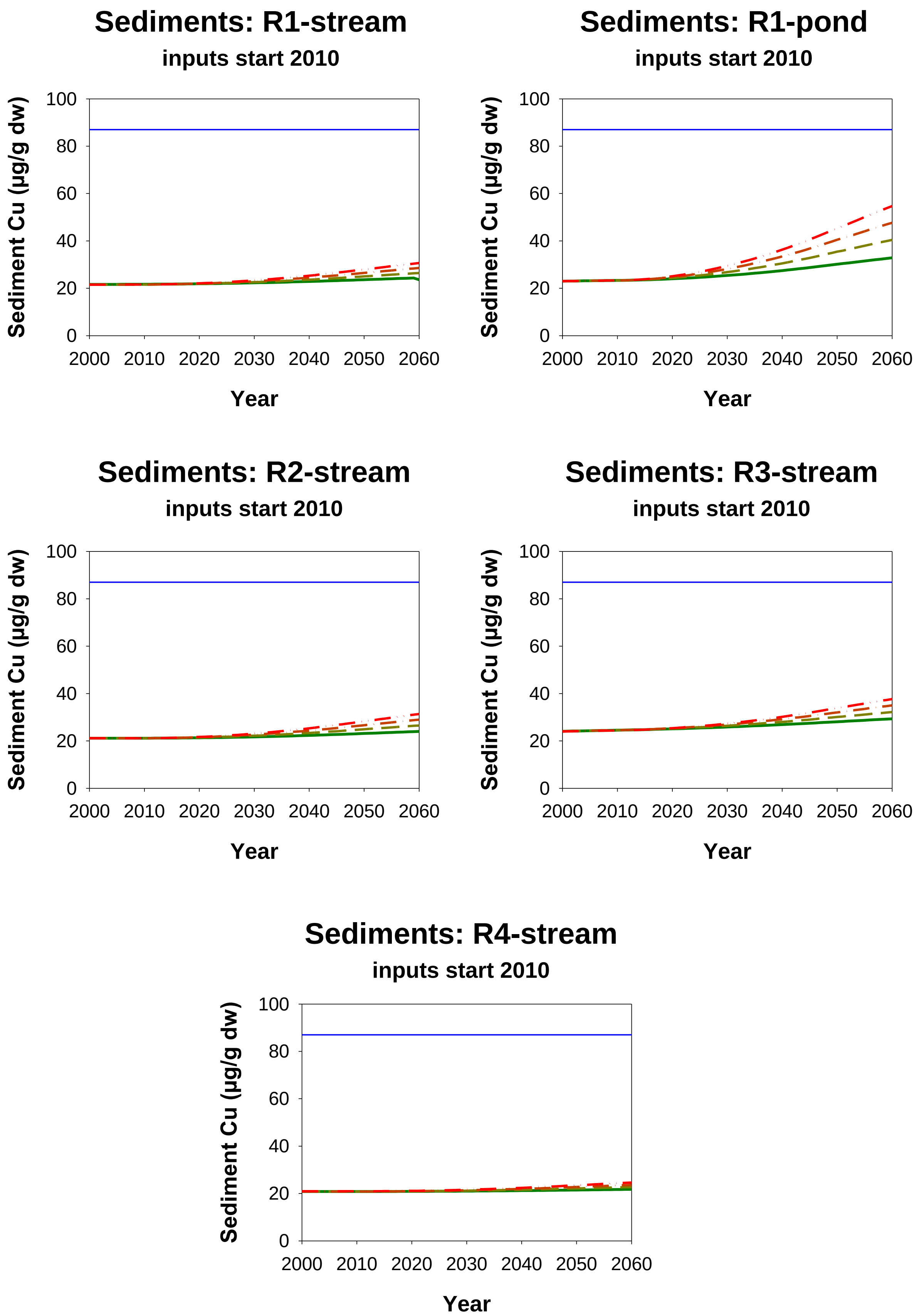


Figure A7-8. Copper sediment concentrations for scenarios R1-R4.

Appendix 8: Charts of copper concentrations in topsoils, surface waters and sediments, in the presence of 10m and 20m vegetation filter strips

Charts show the evolution of predicted copper concentrations from 1850 (representing pre-contamination conditions) to 2060. Concentrations resulting from specific application rates are denoted as follows on the charts:

2 kg Cu ha_{-1} a_{-1} Solid green line
4 kg Cu ha_{-1} a_{-1} Dashed yellow line
6 kg Cu ha_{-1} a_{-1} Dash-dot orange line
8 kg Cu ha_{-1} a_{-1} Dash-dot-dot red line

On each chart, the relevant copper PNEC is indicated by a solid horizontal blue line. On the chart displaying the simulations of surface water concentrations, the 'reasonable' worst case' PNEC of 6.8 µg l^{-1} is displayed as a dashed horizontal blue line, and the proposed EU RAC of 9.5 µg l^{-1} is displayed as thick red line.

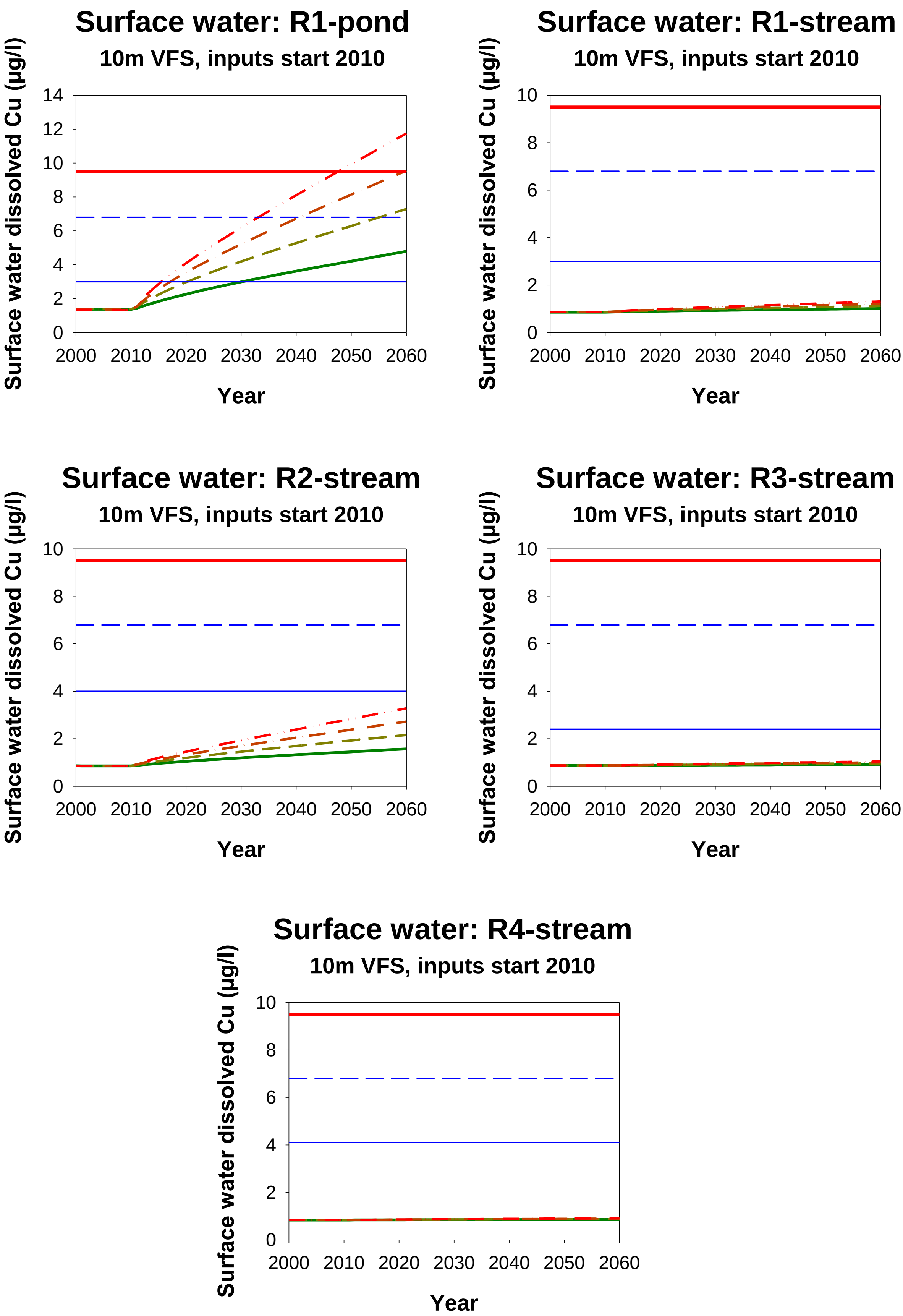


Figure A8-1. Surface water copper concentrations for scenarios R1 to R4, assuming VFS of 10m width.

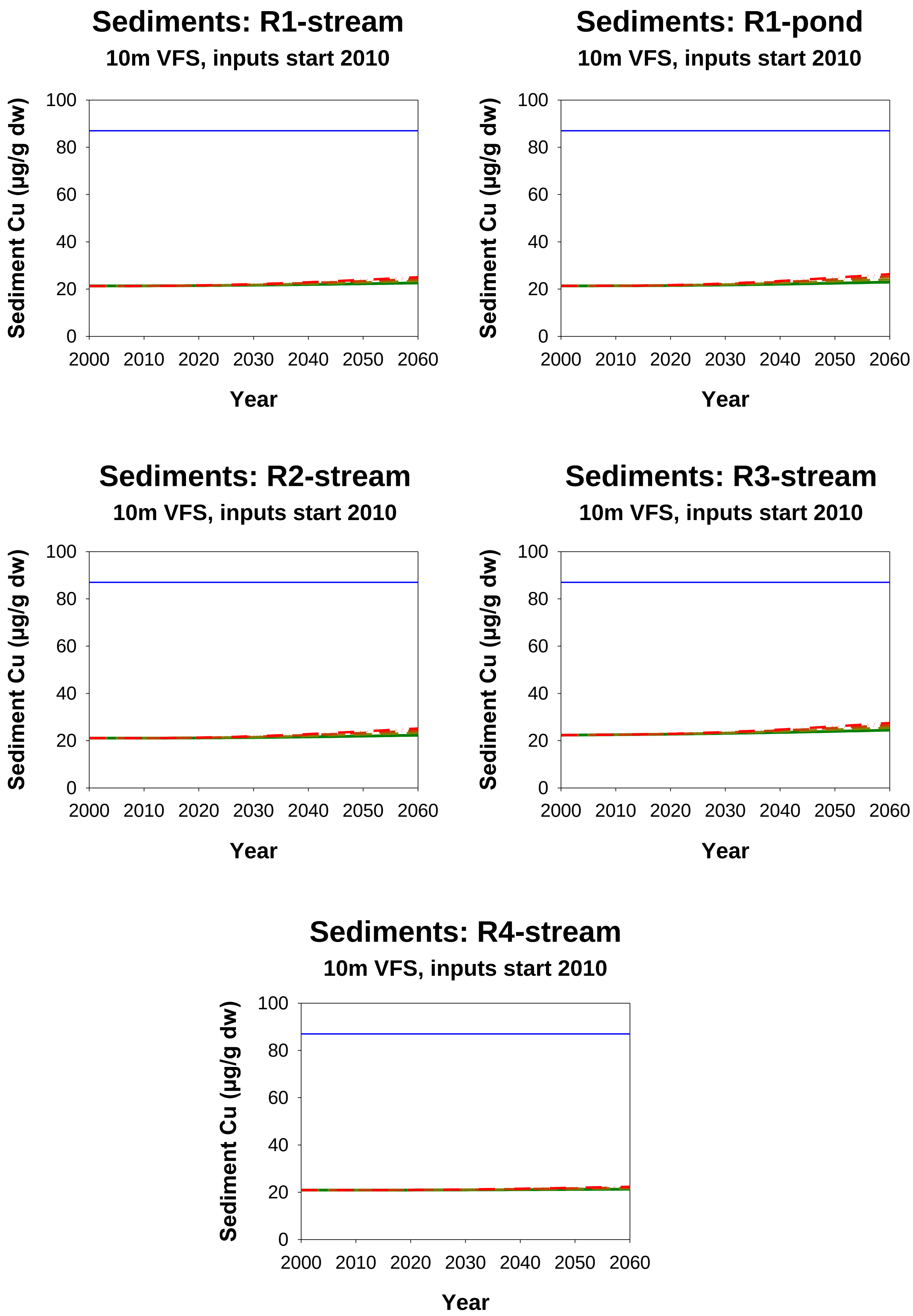


Figure A8-2. Sediment copper concentrations for scenarios R1 to R4, assuming VFS of 10m width.

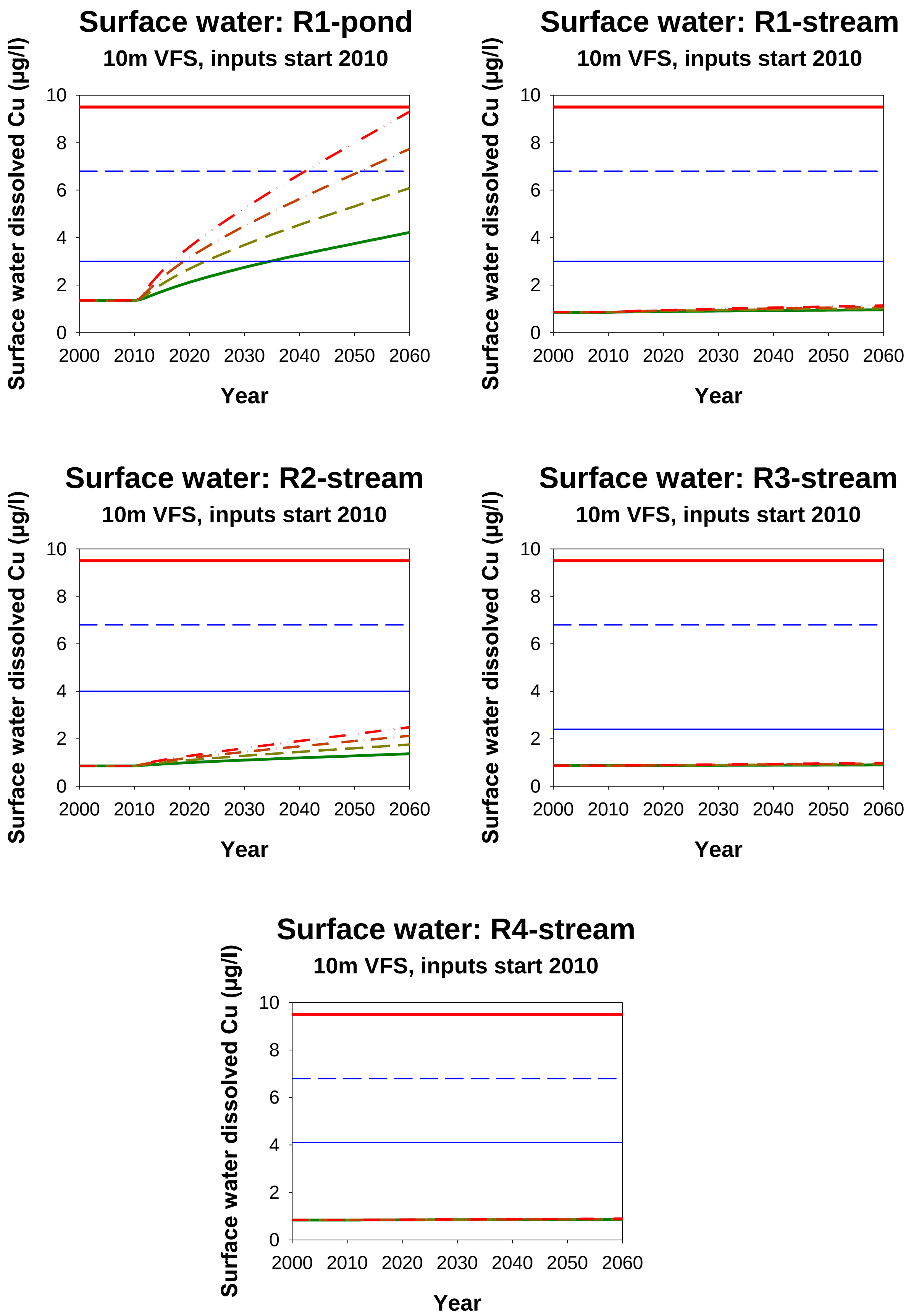


Figure A8-3. Surface water copper concentrations for scenarios R1 to R4, assuming VFS of 20m width.

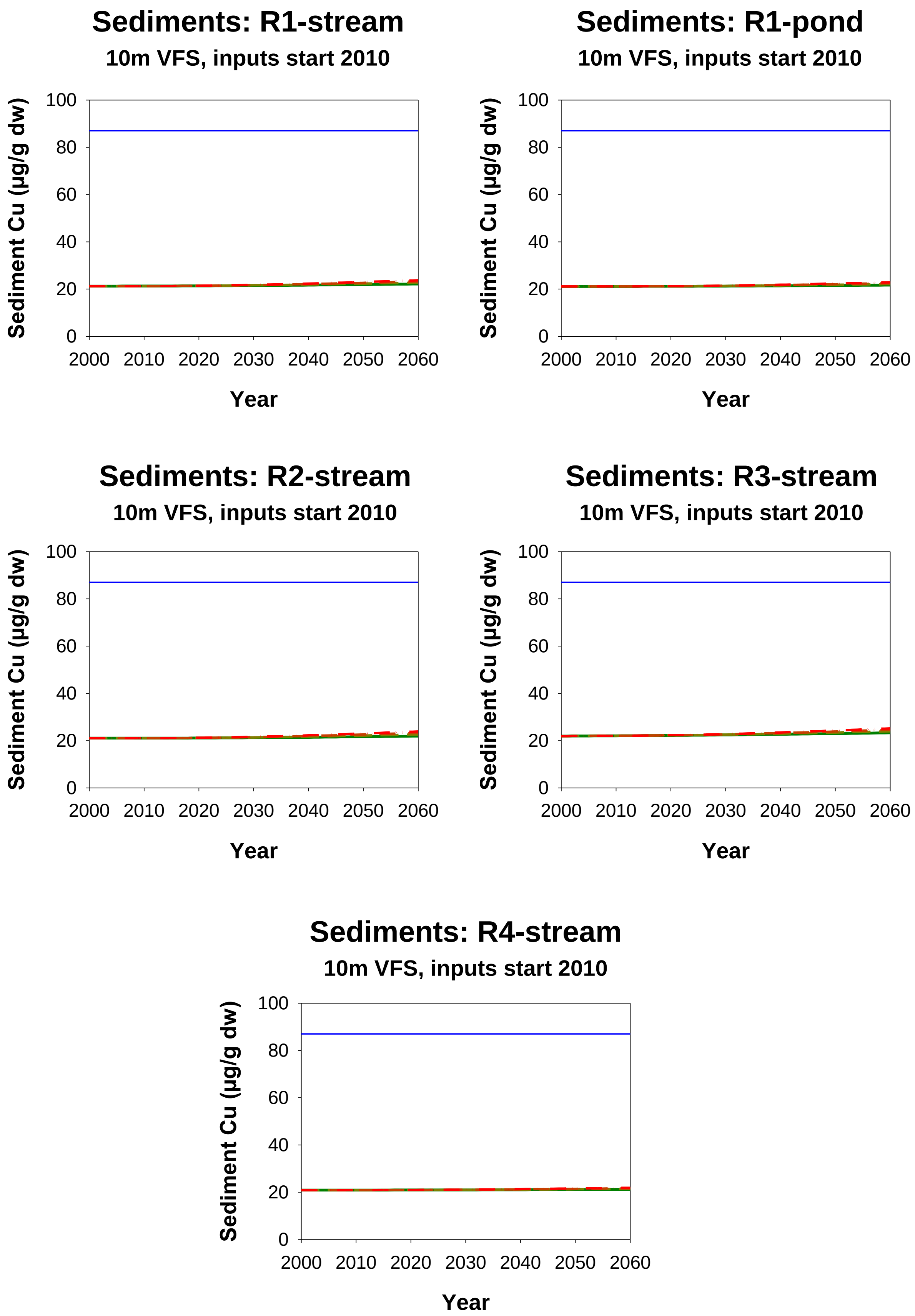


Figure A8-4. Sediment copper concentrations for scenarios R1 to R4, assuming VFS of 20m width.

Appendix 9: Charts of copper concentrations in surface waters and sediments, illustrating the influence of simulating vegetation filter strips

Charts show the predicted copper concentrations in either surface waters or sediments in 2030, under the three scenarios for the simulation of vegetation filter strips (VFS):

No VFS: Unshaded (white) bars
10m wide VFS: Light shaded (grey) bars
20m wide VFS: Dark shaded (dark grey) bars

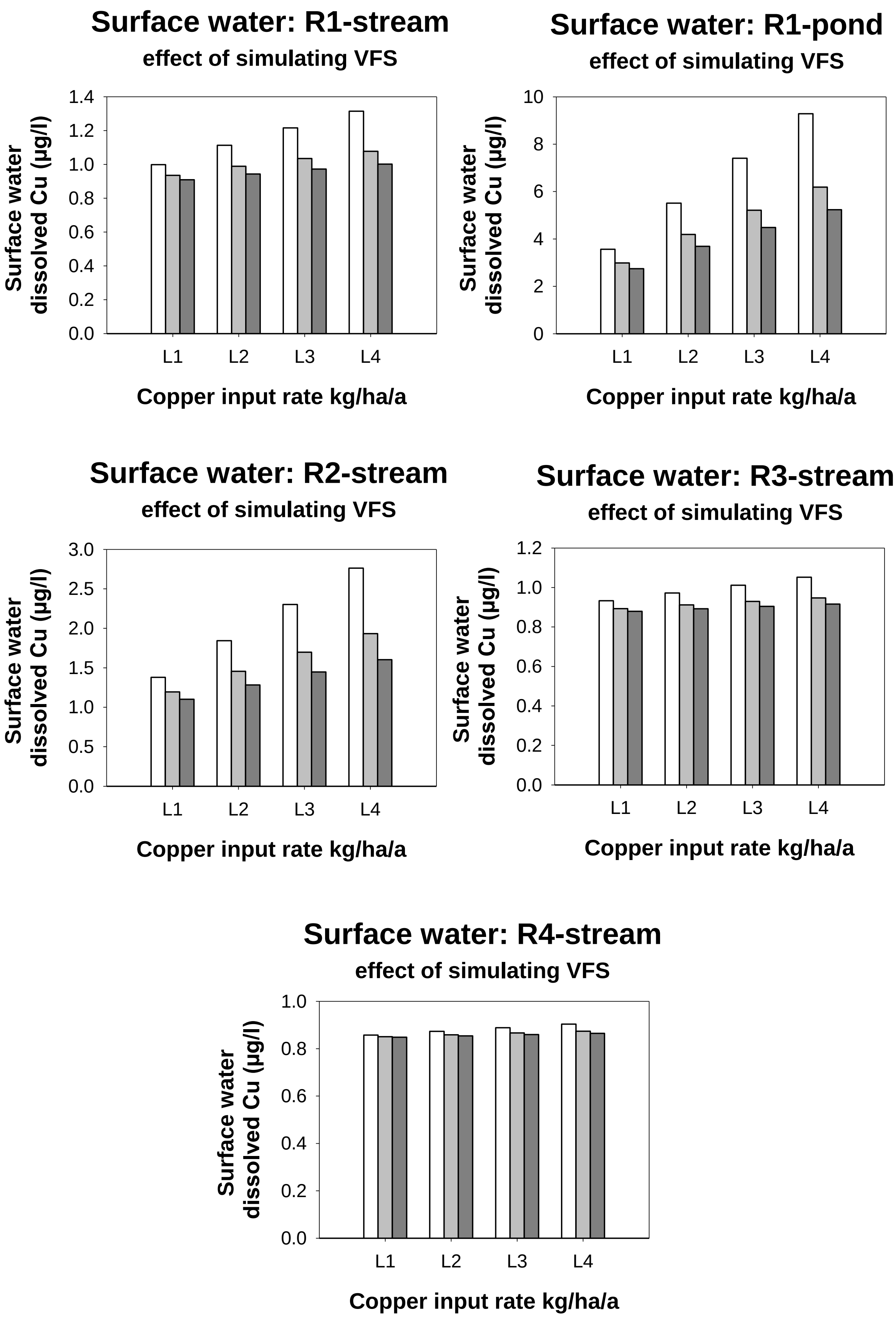
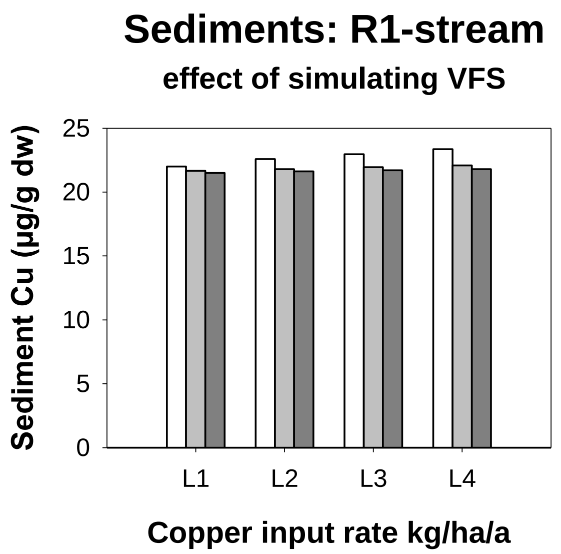
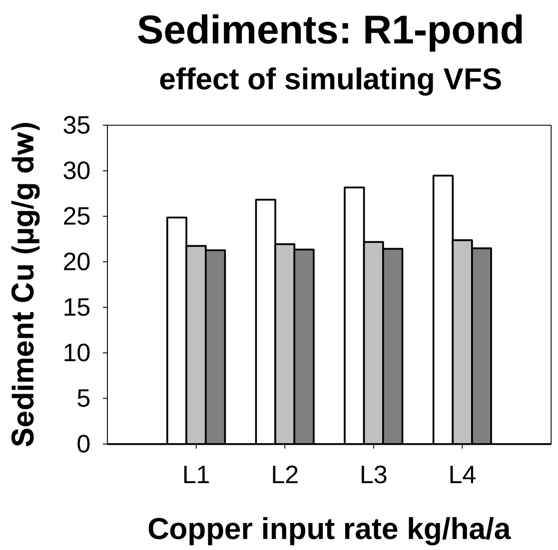
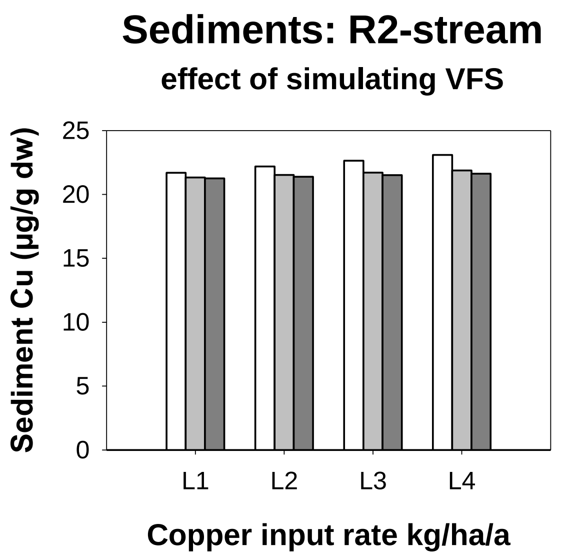
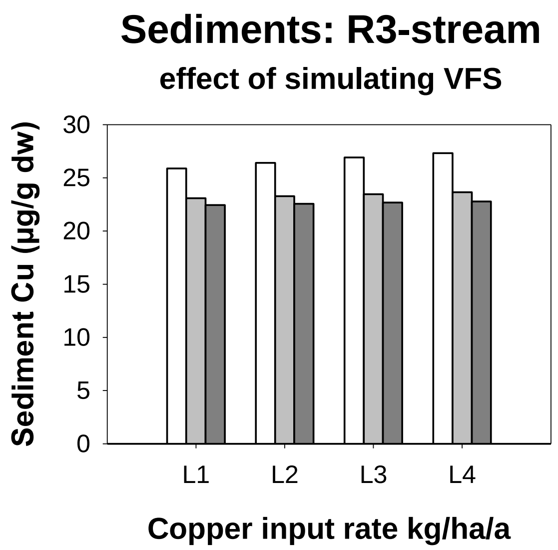


Figure A9-1. Predictions of copper concentrations in surface waters of the runoff scenarios in 2030.









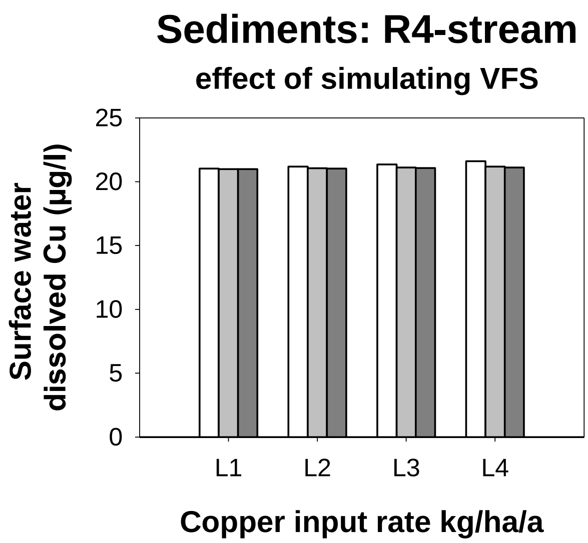


Figure A9-2. Predictions of copper concentrations in sediments of the runoff scenarios in 2030.

Appendix 10: Table and charts of the predicted distribution of copper in surface waters in 2030

The charts show the predicted distribution of copper in surface waters of each scenario in 2030, in response to a loading rate of 8 kg Cu ha^{-1} a^{-1}. Four forms of copper are identified in the charts: free ion, dissolved inorganic complexes, dissolved organic complexes and in suspended sediment.

Free ion: white bars
Dissolved inorganic complexes: black bars
Dissolved organic complexes: light grey bars
Suspended sediment: dark grey bars

Table A10-1. Predictions of the distribution of copper in surface waters in 2030 in response to a loading rate of 8 kg Cu ha^{-1} a^{-1}.

FI = free ion; DI = dissolved inorganic complexes; DO = dissolved organic complexes; SED = suspended sediment-bound. The values are percentages of the total surface water copper.

		no attenuation				10 m wide VFS				20m wide VFS			
		FI	DI	DO	SED	FI	DI	DO	SED	FI	DI	DO	SED
D1	Ditch	<0.1	0.1	49.8	50.1								
	Stream	<0.1	0.1	49.9	50.0								
D2	Ditch	<0.1	0.3	14.2	85.5								
	Stream	<0.1	0.3	14.6	85.1								
D3	Ditch	<0.1	0.5	31.5	68.0								
D4	Pond	<0.1	0.2	44.2	55.6								
	Stream	<0.1	0.2	44.8	55.0								
D5	Pond	<0.1	0.6	11.4	88.0								
	Stream	<0.1	0.6	11.4	88.0								
D6	Ditch	<0.1	0.9	4.2	94.9								
R1	Pond	<0.1	0.9	7.6	91.8	<0.1	0.5	7.5	92.0	<0.1	0.5	7.4	92.0
	Stream	<0.1	3.3	8.9	87.8	<0.1	2.4	8.6	89.0	<0.1	2.0	8.5	89.5
R2	Stream	0.2	0.4	16.1	83.3	0.1	0.3	15.7	83.8	<0.1	0.3	15.4	84.1
R3	Stream	<0.1	0.3	8.0	91.7	<0.1	0.3	7.9	91.8	<0.1	0.3	7.9	91.9
R4	Stream	<0.1	0.1	7.3	92.6	<0.1	0.1	7.3	92.6	<0.1	0.1	7.3	92.6

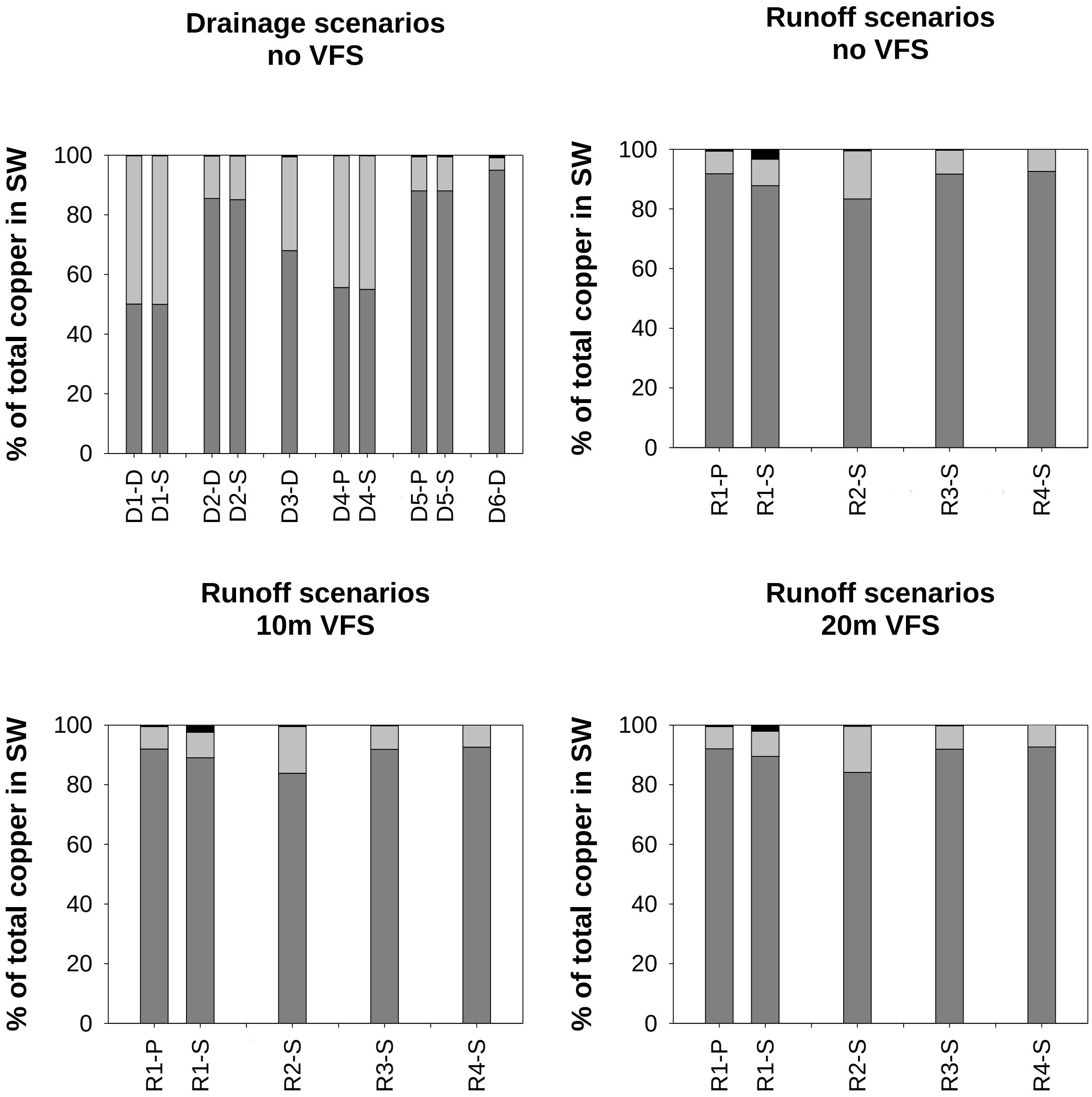


Figure A10-1. Predictions of the distribution of copper in surface waters in 2030 in response to a loading rate of 8 kg Cu ha^{-1} a^{-1}.

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