# The impact of climate change on aquatic risk from agricultural pesticides in the US

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**Abstract**

Agricultural pesticides have adverse impacts on water quality and aquatic species. These impacts are sensitive to climate because pest pressure and corresponding pesticide application rates vary with weather and climate conditions. In this paper, we investigate how climate change affects the acute and chronic toxicity risk to algae, daphnia, and fish from the ten most hazardous pesticides in twelve coastal states of the US. We combine climate change projections from the Canadian and Hadley climate model, statistically estimated dependencies of pesticide applications to climate and weather variables, and the environmental risk indicator REXTOX developed by the OECD. On average, we find that climate change is likely to increase the toxicity risk to aquatic species because of increased application of agricultural pesticides. Algae appear to be the most negatively affected category. Across five broad crop groups, pesticide use on fruits and vegetables contributes the most to increased aquatic pollution. Within the twelve coastal states, the highest impacts are found in Texas, Florida, California, South and North Carolina.

KEY WORDS**:** climate change scenarios, agricultural pesticides, acute toxicity, chronic risk, aquatic species, marine environment, United States.

# 1 Introduction

At the beginning of the twentieth century, society began to face the problem of global warming a development which may affect all economic sectors but especially agriculture. Many studies investigate the agricultural effects of climate change (Kaiser et al. 1995, Lewandrowski et al. 1999, Adams et al. 1990). Across these studies, there is broad agreement that climate changes will have substantial ramifications for US agriculture. Uncertainty and concern exists about the impacts of climate change on pesticide applications. Chen et al. (2003) study the relationship between pesticide and climate in US agriculture with a statistical model. Their results suggest that climate change will increase pesticide use in US agriculture. Mainly comprised of plant protection products, pesticides are designed to control harmful organisms by influencing their ability to live. Currently, pesticides are employed on a large scale and generally considered as indispensable in modern farming. They have contributed to increased crop yields, more uniform product quality, and reduced post harvest losses. However, their biocidal characteristics may endanger aquatic ecosystems and diminish the quality of water suppliers.

Pesticides can migrate from agricultural fields into the aquatic environment through surface, subsurface, and groundwater flows and subsequent river transport (Richards et al. 1987; Pereira et al. 1993, Schulz 2001, Flury et al. 1996, Battaglin et al. 2003). Regular inflow and high persistence can result in high pesticide concentrations in surface waters over weeks and months (Groenendijik et al. 1994, Beketov et al. 2008, Dores et al. 2001). Their influences on aquatic species include direct killings (Pimentel 2005; Erdogan et al. 2007, Perschbacher et al. 2008), functional disorders and reproductive abnormalities (Henny et al. 2008, Hontela et

al. 2008, Moore et al. 2007, Boone 2008), and adverse impacts on prey species (Kim et al. 2008, Couillard et al. 2008).

In recognition of these adverse impacts, the US has implemented extensive legal changes over the last decades to control and regulate the use of pesticides. However, despite more restrictions, pesticide residuals still remain at detectable levels in the aquatic environment. Recent studies of major rivers and streams in the US document that 96 percent of all fish samples, 100 percent of all surface water samples, and 33 percent of major aquifers contained at least one pesticide at detectable levels (EPA, 1999). Adverse impacts of agricultural pesticides on non-target organisms are evaluated through risk indicators. The risk assessment for the aquatic environment involves a comparison of estimated exposure to pesticides in surface waters to toxic concentrations which are known from experiments.

The potential change in pesticide applications due to climate change may have substantial impacts on aquatic ecosystems. In this paper, we quantify the resulting change in risk for aquatic species. We employ the aquatic risk indicator REXTOX (OECD, 2000) to estimate changes in potential exposure and risk for species in the aquatic environment of US coastal states. The REXTOX indicator is computed for estimated changes in pesticide application under Canadian and Hadley climate model based scenarios.

The paper proceeds as follows. Section 2 describes the data. Section 3 presents the basic model equations. The sensitivity of aquatic species to climate change induced changes in pesticide application is analyzed in section 4. Finally, section 5 concludes.

# 2 Empirical Data

The availability, reliability, and completeness of input data determine the quality of the REXTOX results. The REXTOX, considers 150 active ingredients which are the most frequently detected pesticides in water bodies in coastal region of US states.

State-level data on pesticide usages for agricultural food products from 1990 to 2004 were obtained from the Agricultural Chemical Usage survey (NASS ,2005. Agricultural Chemical Usage.). These data include statistics on pesticide applications covering 335 active ingredients, 12 US states, 54 crops, and 14 years. The survey contains information on application rate, treated area, recommended number of applications, and actual dose rate for each pesticide. Crops are classified in five groups (Table 1). Furthermore, data on the proportion between surface water area and planted area were obtained from the 1997 National Resources Inventory (USDA, 1997)

Data on chemical properties and the environmental fate related to degradation pathways, half-life, and Organic Carbon Absorption coefficient (Koc) for the studied pesticides were obtained from a USDA database (ARS, 2002). This database on pesticide properties was "developed to provide water quality modelers and managers with a list of the pesticide properties most important for predicting the potentials of pesticides to move into ground and surface waters" (ARS, 2002). The ARS database has two major advantages over other sources: 1) references are given for all values and 2) all data have been verified and their accuracy confirmed by manufacturers.

Toxicity values are an important component for the REXTOX indicator calculation. Misspecifications can severely bias the value of this indicator and the relative contribution of

individual pesticides to overall environmental risk. For several active ingredients, toxicity parameters differed considerably across commonly referenced data sources. In addition, the median toxicity endpoint (EC50) and lethal (LC50) concentration rates differ for some chemical compounds. These differences may in part be explained by inconsistent endpoint measurements. For active ingredients, for which EC50 or LC50 values were not available, "No Observed Effect Concentrations" (NOEC) were used. Exact values for chronic or long-term toxicity were not available for all active ingredients. Sometimes, these values are given as lower bounds (e.g. NOEC (96h) >100mg/L). The data on pesticide toxicity values were obtained from the Pesticide Action Network Database (PAN Pesticides Database 2007).

## 3 Model description

The risk assessment for pesticides in the aquatic environment relies on a comparison between estimated exposure concentrations in surface water bodies and endpoints from a series of effect tests. A variety of aquatic risk assessment models have been developed, ranging from simple empirical models to comprehensive, physics-based distribution models that require complex parameterizations (Kellogg 2000, Schuler et al. 2008, Probst et al. 2005, Junghans et al. 2006, Renaud et al. 2008, Ritter et al. 2004, Cheplick et al. 2004, Carsel et al. 1985, Arnold et al. 1998, Borah et al. 2004, Zhou et al. 2008). None of these models of pesticide risk assessment can be considered universally valid. Uncertainty about the accuracy of model results relates to the adequacy of model equations and input parameters.

In light of the above mentioned uncertainties, the OECD designed and developed risk assessment tools for national authorities to monitor progress of measures designed to reduce the environmental risk from pesticide use and to plan pesticide management regulations. Several countries including Switzerland, Germany, Sweden, The Netherlands, and Japan

tested and validated the OECD methodology with their own input data. The reports of these countries suggest that the methodological tools can be adapted to different regional conditions including weather, soil, and landscape features. The OECD tools consist of three aquatic risk indicators: ADSCOR; SYSCOR; and REXTOX. The most important difference between these three indicators relates to their representation of exposure, the amount of pesticide that ends up in surface waters. All three indicators consider the crop, the amount of pesticide used, how the pesticide is applied, the mobility and persistence of the pesticide, and environmental factors. However, the functional relationships between these variables differ. Particularly, ADSCOR (ADditive SCORing) converts the value for each variable into a score reflecting its general risk contribution, and then combines these scores by addition. SYSCOR (SYnergistic SCORing) links the variables in a hierarchy reflecting both their importance and their interaction to generate scores which are then added together. REXTOX (Ratio of EXposure to TOXicity) is entirely mechanistic and integrates the actual data through a series of mathematical equations that mirror scientific understanding of the environmental processes that contribute to risk. In this analysis, we employ REXTOX to assess the impacts of changes in pesticide applications in response to climate change.

Table 2, summarizes all variables involved in REXTOX. As shown, REXTOX combines pesticide properties and pesticide use data such as applied dose rate, frequency of application, and method of application with environmental and physical parameters such as soil type, slope, precipitation, water index, water depth and fate properties.

The estimation of REXTOX consists of tree parts. The first part includes a calculation of pesticide losses that are expected to reach surface water bodies. Note that this calculation only accounts losses due to spray drift and runoff because they are considered to be the main

pathways for surface water pollution. The second part computes exposure in surface waters. For REXTOX, exposure can be calculated in three different ways. In the first method (Exposure potential), exposure is calculated based on the recommended pesticide dose rate. In the second method (Exposure unscaled), exposure is calculated based on actual dose rates, or the amount farmers have actually applied, often lower than recommended rates and the number of applications. In the third method (REXTOX scaled), the exposure calculations from second method (REXTOX unscaled), are extended with basic area treated or the total area receiving at least one pesticide treatment. Thus in the third level Rextox scaled is downscaled to the regional or national level. For this study, we consider the third method for exposure calculation so called Exposure scaled as the most extended of available use data and the most appropriate for our approach. In the last part exposure is divided by the appropriate toxicity value to obtain the risk index of REXTOX. All above mentioned risk indices are calculated as acute (short-term, hours) and chronic (long-term, days) values. Acute risk indices correspond to the LC50 value, i.e. the concentration that would be lethal to 50 out of 100 exposed individuals. Long-term risk indices are based on NOEC (Non observed effect concentrations) thresholds. All aquatic species are represented by three main groups: Algae, Daphnia, Fish (OECD, 2000). More details on individual equations appear in Appendix 1.

While including precise information on spray drift and runoff, REXTOX ignores altogether other routes of potential aquatic exposure. This makes the use of this indicator less suitable for pesticides which are expected to be very mobile through the soil. Furthermore, there is no account of pesticides applied through seed treatment or fertilization. Thus, the values produced by REXTOX may somewhat underestimate the real risk.

The estimation of climate change impacts on pesticide concentrations in the aquatic environment involves several steps. First, scenario projections from the Canadian and Hadley climate models are downscaled to obtain regional changes in relevant weather and climate parameters. Second, for each scenario, changes in pesticide applications are computed by updating climate and weather parameters of an econometric model (Koleva et al. 2009). Third, scenario specific changes in pesticide applications are used to recalculate REXTOX.

## 4 Results

Adjustments in pesticide applications in response to climate change are shown in Figures 1 to 3. For both the Canadian and the Hadley climate model, the application of most pesticides will increase. In many US states, the pesticide application rates increase between 18 and 28 percent by 2100 (Figure 1). However, the climate change impacts on application rates differ considerably across pesticides. While the majority of chemical classes increase, triazine, neonicotinoid and inorganic pesticides decrease (Figure 2). Figure 3, displays changes in pesticides application for individual crop types. The highest increase is found for cereals with 26 percent for Hadley and 28 for Canadian climate change scenarios until 2100. For the other crop types, we estimate increases in pesticide application rates up to 16 percent.

The climate change scenario based projections for pesticide applications are used to incorporate with the REXTOX indicator. For our approaches we consider base scenario, which is the average of REXTOX under current climate or REXTOX base on the observed pesticides application, Canadian and Hadley climate change scenarios in three time period 2030, 2070 and 2100. We analyze aquatic risk changes across the states, changes in risk contribution across the pesticides and risk indexes by crop type.

Figures 4 to 6 summarize the changes in aquatic risk by US state and aquatic species category. These changes are aggregated over individual pesticides and crops for projected changes in whether and climate parameters in 2030, 2070, and 2100. All values are relative to the base year 2000. The scenario differences between the Canadian and Hadley climate projections are fairly small and do not exceed four percent. More detailed implications of projected 2100 climate conditions are displayed in Appendix 2. If not indicated our results refer to the Hadley center's climate projections. Results show that the projected change in weather and climate will increase average risk for all aquatic species categories between 16 and 26 percent. These increases apply both to chronic and acute toxicity. However, the contributions from individual states to changes in aquatic toxicity risk vary substantially. Particularly, we find Texas agriculture to cause considerable increases in acute toxicity risk for fish and daphnia over all examined periods. By 2100, the acute toxicity risk from increased pesticide use in Texas will increase by 21 percent for daphnia (Figure 5) and fish (Figure 6). Considerable increases in chronic toxicity risk for fish and daphnia are found for South and North Carolina, Texas, Florida, and California. In North Carolina, we find the highest chronic fish toxicity risk increase amounting to 22 percent in 2100. Similarly, pesticide application changes in South Carolina result in the highest increase of chronic daphnia toxicity amounting to 23 percent in 2100. Across the examined US costal states, we find algae to be the most vulnerable aquatic species category to climate change (Figure 4). In most states, the corresponding increase in relative toxicity risk by 2100 exceeds that for other aquatic species categories. While the highest increase in acute toxicity risk occurs in Florida with 27 percent, the highest increases in chronic toxicity risk are found in California with 26 percent and Florida and South Carolina with 25 percent (Figure 4).

Aquatic risk impacts differ substantially across active ingredients of pesticides. Table 3 lists the ten most risk increasing pesticides for each aquatic species category, for acute and chronic toxicity, and for both climate model projections. The values represent relative changes to the base period and are aggregated over US states and crops. The shown pesticides are ranked according to their impact on aquatic risk with rank 1 representing the highest risk change. Note that the order of pesticides is the same for the Canadian and Hadley scenarios. Several pesticides from the top ten list are found in each aquatic species category both for acute and chronic toxicity. Particularly, increased application of maneb, mancozeb, lambda-cyhalothrin, and permethrin cause substantial increases in aquatic toxicity risk (Table 3). While the percentage changes of some pesticides are relatively similar across aquatic species categories, there are differences in corresponding rank. For example, mancozeb increases the aquatic risk across aquatic species categories consistently between 36 and 41 percent by 2100 for both climate model projections. However, while this pesticide is the second most influential driver for acute algae toxicity, it ranks $5^{th}$ and $4^{th}$ place for acute and chronic daphnia toxicity, and $4^{th}$ and $2^{nd}$ place for acute and chronic fish toxicity, respectively. Similar results are observable for lambda-cyhalothrin, permethrin (Table 3).

Other pesticides have the same rank in ten top lists among the aquatic species category but differ in their relative impact on aquatic risk. For instance, methamidophos, ranks first in each aquatic species category for acute and/or chronic toxicity, but their contributions to changes in risk vary between 42 and 46 percent (Table 3). Furthermore, for several of the top ten pesticides, we find diverse responses to different aquatic species categories. For instance, dimethoate increases the chronic fish toxicity risk by 31 percent (Canadian climate projection) and 29 percent (Hadley climate projection). However, all the other aquatic toxicity risk categories remain relatively unaffected (Table 3). For some pesticides we find no

changes in risks as climate change. Appendix 3, lists this pesticides by aquatic species category and toxic effects.

Figures 7-8 show, changes in aquatic risk from individual crop types aggregated over pesticides and US states. All values represent percentage changes in aquatic risks to the base period in 2030, 2070, and 2100 for Hadley climate model. The values across the two climate scenarios differ only moderately. For all projected periods we find increase of risk contribution from all crop types in each aquatic species category. Results indicate that the different crop types have different risk contributions to the aquatic species. For Hadley climate model at the end of projected period (2100), we find an increase from 5 to 24 percent for the acute risks (Figure 7) and from 8 to 23 percent for chronic risks (Figure 8) across aquatic species category. Among the crops, we find fruits and vegetables to have the highest risk contribution for all aquatic species in both toxicity classes for Hadley climate model in each projected period. Algae are the most influenced aquatic species category. Both fruits and vegetables contributed to the acute risks increase by 24 percent (Figure 7), and 21 to 22 percent for chronic toxicity for algae in 2100 (Figure 8). Fruits and vegetables will cause substantial acute risk changes for the other aquatic species as well. Figure 7, shows an increase for risks by 21 percent from fruits and by 23 percent from vegetables both for daphnia and fish in 2100 under Hadley climate change scenarios. Considerable risk contribution from fruits we find for chronic toxicity risks (Figure 8) as well. For both aquatic specie categories the risks will increase by 23 percent in 2100.

The lowest risk changes we estimated with root crops from 5 to 9 percent (Figure 7) for acute risks, for all aquatic species, in 2100. The results for chronic risks indicate an increase

by 11 percent for algae, by 9 percent for daphnia, and by 8 percent for fish in the last projected period under Hadley climate scenario (Figure 8).

Despite, the results from Koleva et al., 2009 that reported climate change to influence mostly the pesticides applied on cereals (Figure 3) we find relatively low contribution to the risk changes from cereals. Again the algae are the most influenced category both for acute and chronic toxicity for all projected periods. We find an increase of acute risk for algae by 15 percent (Figure 7) and by 18 for chronic risk. For fish and daphnia under Hadley climate scenarios in 2100 the risks are projected to increase by 12 percent for acute and 14 to 15 percent for chronic toxicity (Figure 8).

# 5 Conclusions

This study employs the risk assessment indicator REXTOX to compute the impact of climate change induced adjustments of pesticide applications on the aquatic environment. The results show noticeable changes both in acute and chronic risk. We find that climate change impacts on agricultural pesticides vary and hence, their contribution to changes in aquatic toxicity risk differs. Because different crops require different pesticides, the contribution also differs across crops. For all major crop types, our analysis shows that the aquatic risk contribution is likely to increase under climate change. Pesticides applied to fruits and vegetables contain the most harmful substances for aquatic species and they have the main contribution in risks increase as climate changes.

Our results have important research and policy implications. First, our estimates can help to improve the mathematical representation of external impacts from agricultural pesticide use in integrated assessment models. These models are increasingly used for the design and

justification of climate and other environmental policies. Second, if the overall external effects of agricultural pesticides are indeed negative the socially optimal response to climate change moves away from adaptation towards mitigation. Third, our results could affect agricultural research programs because the expected social returns to research on alternative pest control strategies would depend on the expected external cost change. Particular, fruits and vegetables may cause substantial environmental damages. Furthermore, our results may have important implications for the design of future crop insurance programs.

Several important limitations and uncertainties to this research should be noted. First, the projections of pesticide applications under climate change are based on statistically estimated dependencies of pesticide applications on weather and climate variables and on model based climate simulations. Thus, the certainty of the estimates presented here depends on the quality and certainty of the underlying models. Second, meaningful variation in $CO_2$ levels is not observable in the data for the climate change effects on pesticides use. Third, the estimates of risk indexes generated by the REXTOX do not include all routes of potential aquatic exposure. Fourth, the states data from NASS and toxicity data from PAN pesticides database we have used may differ in quality and scope across space and time. Therefore, these results might overestimate the impacts of climate change on pesticides application and risk to the aquatic environment.

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# References

Adams,R.M., C.Rosenzweig, R.M.Peart, J.T.Ritchie, B.A.Mccarl, J.D.Glyer, R.B.Curry, J.W.Jones, K.J.Boote, and L.H.Allen. 1990. "Global Climate Change and United-States Agriculture." *Nature*. 345:219-224.

Arnold,J.G., R.Srinivasan, R.S.Muttiah, and J.R.Williams. 1998. "Large area hydrologic modeling and assessment - Part 1: Model development." *Journal of the American Water Resources Association*. 34:73-89.

Battaglin,W.A., E.M.Thurman, S.J.Kalkhoff, and S.D.Porter. 2003. "Herbicides and transformation products in surface waters of the Midwestern United States." *ournal of the American Water Resources Association*. 39:743-756.

Beketov,M.A. and M.Liess. 2008. "Potential of 11 pesticides to initiate downstream drift

of stream macroinvertebrates." *Archives of Environmental Contamination and oxicology*. 55:247-253.

Boone,M.D. 2008. "Examining the single and interactive effects of three insecticides on amphibian metamorphosis." *Environmental Toxicology and Chemistry*. 27:1561-568.

Borah,D.K. and M.Bera. 2004. "Watershed-scale hydrologic and nonpoint-source ollution models: Review of applications." *Transactions of the Asae*. 47:789-803.

Carsel,R.F., L.A.Mulkey, M.N.Lorber, and L.B.Baskin. 1985. "The Pesticide Root Zone Model (Przm) - A Procedure for Evaluating Pesticide Leaching Threats to Groundwater." *Ecological Modelling*. 30:49-69.

Chen,C.C. and B.A.Mccarl. 2003. "An investigation of the relationship between pesticide usage and climate change (vol 50, pg 475, 2001)." *Climatic Change*. 61:250.

Cheplick,J., A.Ritter, W.Williams, and N.J.Snyder. 2004. "Watershed modeling linking PRZM with RIVWQ." *Abstracts of Papers American Chemical Society*. 228:U107-U108.

Couillard,C.M., M.Lebeuf, B.Legare, and S.Trottier. 2008. "Effects of diazinon on mummichog (Fundulus heteroclitus) larvae produced from eggs differentially reated with PCB126." *Archives of Environmental Contamination and Toxicology*. 4:283-291.

Dores,E.F.G.D. and E.M.Lamonica-Freire. 2001. "Aquatic environment contamination by pesticides. Case study: Water used for human consumption in Primavera do Leste, Mato Grosso - Preliminary analyses." *Quimica Nova*. 24:27-36.

Erdogan,O., M.Atamanalp, T.Sisman, E.Aksakal, and G.Alak. 2007. "Effects of 2,2-dichlorovinyl dimethyl phosphate (DDVP) on Hsp70 gene expression in rainbow trout." *Israeli Journal of Aquaculture-Bamidgeh*. 59:230-234.

Flury,M. 1996. "Experimental evidence of transport of pesticides through field soils - A review." *Journal of Environmental Quality*. 25:25-45.

Groenendijk,P., J.W.H.Vanderkolk, and K.Z.Travis. 1994. "Prediction of Exposure Concentrations in Surface Waters." *Freshwater Field Tests for Hazard Assessment of Chemicals*.105-125.

Henny,C.J., T.W.Anderson, and J.J.Crayon. 2008. "Organochlorine pesticides, polychlorinated biphenyls, metals, and trace elements in waterbird eggs, Salton Sea, California, 2004." *Hydrobiologia*. 604:137-149.

Hontela,A., V.S.Leblond, and J.P.Chang. 2008. "Purification and isolation of corticosteroidogenic cells from head kidney of rainbow trout (Oncorhynchus mykiss) for testing cell-specific effects of a pesticide." *Comparative Biochemistry and Physiology C-Toxicology & Pharmacology*. 147:52-60.

Junghans,M., T.Backhaus, M.Faust, M.Scholze, and L.H.Grimme. 2006. "Application and validation of approaches for the predictive hazard assessment of realistic pesticide mixtures." *Aquatic Toxicology*. 76:93-110.

Kaiser,H.M. and P.Crosson. /8. "Implications of Climate Change for U.S. Agriculture." *American Journal of Agricultural Economics*. 77:734-740.

Kellogg,R.L., R.F.Nehring, A.Grube, D.W.Goss, and S.Plotkin. 2002. "Environmental indicators of pesticide leaching and runoff from farm fields." *Agricultural Productivity: Measurement and Sources of Growth*. 2:213-256.

Kim,Y., J.Jung, S.Oh, and K.Choi. 2008. "Aquatic toxicity of cartap and cypermethrin to different life stages of Daphnia magna and Oryzias latipes." *Journal of Environmental Science and Health Part B-Pesticides Food Contaminants and Agricultural Wastes*. 43:56-64.

Lewandrowski,J. and D.Schimmelpfennig. 1999. "Economic implications of climate change for US agriculture: Assessing recent evidence." *Land Economics*. 75:39-57.

Lutz,W.„Berechnung von hochwasserabflüssen unter anwendung von gebietskenngrößen" Mittlg. Inst. Hydrologie Wasserwirtschaft, Univ. Karlsruhe, (1984):Heft 24.

Maniak,U., Regionalisierung von parametern für hochwasserabflußganglinien. In: Kleeberg, H.B. (Ed.), Regionalisierung der Hydrologie. DFG, Mittlg. Senatskomm für Wasserf. 11, (1992): S.325–S.332.

Moore,A., N.Lower, I.Mayer, and L.Greenwood. 2007. "The impact of a pesticide on migratory activity and olfactory function in Atlantic salmon (Salmo salar L.) smolts." *Aquaculture*. 273:350-359.

NASS ,2005. Agricultural Chemical Usage.

OECD, 2000. Report of the OECD Pesticide Aquatic Risk Indicators Expert Group. Braunschweig, Germany, OECD: 14-21

PAN Pesticide Database, 2008. Pesticide Properties Database

Pereira,W.E. and F.D.Hostettler. 1993. "Nonpoint-Source Contamination of the Mississippi River and Its Tributaries by Herbicides." *Environmental Science & Technology*. 27:1542-1552.

Perschbacher,P.W., G.M.Ludwig, and R.Edziyie. 2008. "Effects of atrazine drift on production pond plankton communities and water quality using experimental mesocosms." *Journal of the World Aquaculture Society*. 39:126-130.

Pimentel,D. 2005. "Environmental and economic costs of the application of pesticides primarily in the United States." *Environment Development and Sustainability*. 7:229- 252.

Probst,M., N.Berenzen, A.Lentzen-Godding, and R.Schulz. 2005. "Scenario-based simulation of runoff-related pesticide entries into small streams on a landscape level." *Ecotoxicology and Environmental Safety*. 62:145-159.

Renaud,F.G. and C.D.Brown. 2008. "Simulating pesticides in ditches to assess ecological risk (SPIDER): II. Benchmarking for the drainage model." *Science of the Total Environment*. 394:124-133.

Richards,R.P., J.W.Kramer, D.B.Baker, and K.A.Krieger. 1987. "Pesticides in Rainwater in the Northeastern United-States." *Nature*. 327:129-131.

Riedel,G. and U.Maniak. 1999. "Regionalization of parameters for direct runoff." *Regionalization in Hydrology*.165-170.

Ritter,A.M. and W.M.Williams. 2004. "Watershed modeling by linking PRZM, RICEWQ, and RIVWQ." *Abstracts of Papers of the American Chemical Society*. 228:U97.

Schuler,L.J. and G.M.Rand. 2008. "Aquatic risk assessment of herbicides in freshwater ecosystems of south Florida." *Archives of Environmental Contamination and Toxicology*. 54:571-583.

Schulz,R. 2001. "Comparison of spray drift- and runoff-related input of azinphos-methyl and endosulfan from fruit orchards into the Lourens River, South Africa." *Chemosphere*. 45:543-551.

USDA, 2002. The ARS (Agricultural Research Service) Pesticide Properties Database. Department of Agriculture, United States.

USEPA, 1999. AQUIRE-Aquatic Toxicity Information Retrieval Database. US Environmental Protection Agency, National Health and Environmental Effects Research Laboratory, Duluth, MN.

USDA, 1997. National Resources Inventory Water area.

Zhou,S.J. and S.P.Griffiths. 2008. "Sustainability Assessment for Fishing Effects (SAFE): A new quantitative ecological risk assessment method and its application to elasmobranch bycatch in an Australian trawl fishery." *Fisheries Research*. 91:56-68.

**Table 1    Crop scope and aggregation**

| Cereals | Fruits | Vegetables | Beans | Root crops |
|---|---|---|---|---|
| Corn | Grapefruit | Cucumbers | Beans | Potatoes |
| Rice | Lemons | Eggplant | Soybeans | |
| Spring wheat | Limes | Melons | Peas | |
| Durum wheat | Tangelos | Peas | | |
| Winter wheat | Tangerines | Pecans | | |
| | Temples | Peppers | | |
| | Oranges | Pumkins | | |
| | Blackberries | Squash | | |
| | Blueberries | Tomatoes | | |
| | Raspberries | Asparagus | | |
| | Strawberries | Broccoli | | |
| | Apricots | Cabbage | | |
| | Avocados | Cauliflower | | |
| | Cherries | Collards | | |
| | Grapes | Greens | | |
| | Nectarines | Kale | | |
| | Peaches | Lettuce | | |
| | Plums | Spinach | | |
| | Prunes | | | |
| | Apples | | | |
| | Pears | | | |

**Table 2    REXTOX Parameters**

| Variables | | |
|---|---|---|
| *Pesticides use* | *Environmental factors* | *Pesticides fate* |
| Treated area (acres) | Water index (Wi) (ha) | DT 50, soil (half-life in soil) |
| Recommended dose rate - RDR( kg/ha) | Water depth (m) | Koc( Organic carbon coefficient) |
| Applied dose rate- ADR(kg/ha) | Slope of treated agricultural area | |
| Frequency of treatment per season AFA- number of application | Season mean precipitation per state (inches) | |
| Method of application* | % of organic carbon in the soil | |
| Width of spry drift buffer (m) | Soil type ( Loamy or sandy) | |
| Width of runoff buffer (m) | Crop stage treatments (early/late) | |
| Compliance with of spry drift buffer (0-100%) | Plant interception 0% when crop stage early 70% when crop stage late | |
| Compliance with of runoff buffer (0-100%) | Precipitation (mm) | |

* Ground spray, air blast, areal, granular broadcast, granular incorporated, punning paint, soil sterilant, seed treatment

**Table 3    Relative impact on aquatic toxicity risk of the ten highest ranking pesticides**

| Rank | Acute toxicity risk | | | Chronic toxicity risk | | |
|---|---|---|---|---|---|---|
| | Pesticide | Hadley | Canadian | Pesticide | Hadley | Canadian |
| Algae | | | | | | |
| 1 | Methamidophos | 43 | 42 | Methamidophos | 46 | 46 |
| 2 | Maneb | 40 | 43 | Maneb | 44 | 45 |
| 3 | Metribuzin | 39 | 39 | Metalaxyl | 42 | 40 |
| 4 | Metalaxyl | 38 | 39 | Mancozeb | 40 | 41 |
| 5 | Mancozeb | 37 | 38 | Oxydemeton | 38 | 40 |
| 6 | Oxydemeton | 36 | 37 | Cyfluthrin | 36 | 39 |
| 7 | Cyfluthrin | 35 | 36 | Lambda-cyhalothrin | 33 | 36 |
| 8 | Triadimefon | 32 | 34 | Tebuconazole | 30 | 31 |
| 9 | Lambda-cyhalothrin | 30 | 33 | Fenbuconazole | 28 | 29 |
| 10 | Permethrin | 28 | 31 | Permethrin | 26 | 28 |
| Daphnia | | | | | | |
| 1 | Methamidophos | 42 | 42 | Methamidophos | 43 | 45 |
| 2 | Maneb | 40 | 41 | Maneb | 41 | 41 |
| 3 | Metribuzin | 39 | 40 | Metalaxyl | 40 | 41 |
| 4 | Metalaxyl | 38 | 39 | Mancozeb | 39 | 40 |
| 5 | Mancozeb | 36 | 38 | Oxydemeton | 37 | 39 |
| 6 | Oxydemeton | 34 | 35 | Cyfluthrin | 36 | 37 |
| 7 | Cyfluthrin | 33 | 34 | Lambda-cyhalothrin | 33 | 36 |
| 8 | Triadimefon | 30 | 32 | Tebuconazole | 32 | 32 |
| 9 | Lambda-cyhalothrin | 29 | 29 | Fenbuconazole | 29 | 31 |
| 10 | Permethrin | 27 | 28 | Permethrin | 27 | 28 |
| Fish | | | | | | |
| 1 | Methamidophos | 42 | 43 | Metalaxyl | 40 | 42 |
| 2 | Maneb | 41 | 43 | Mancozeb | 39 | 39 |
| 3 | Oxydemeton | 40 | 41 | Cyfluthrin | 37 | 39 |
| 4 | Mancozeb | 39 | 40 | Lambda-cyhalothrin | 36 | 37 |
| 5 | Cyfluthrin | 37 | 38 | Tebuconazole | 33 | 35 |
| 6 | Fluazifop | 36 | 36 | Fenbuconszole | 31 | 34 |
| 7 | Lambda-cyhalothrin | 34 | 36 | Dimethoat | 29 | 31 |
| 8 | Fenbuconazole | 31 | 32 | Permethrin | 27 | 30 |
| 9 | Permethrin | 29 | 31 | Cymoxanil | 25 | 26 |
| 10 | Thiophanate | 26 | 29 | Thiophanate | 23 | 26 |

**Figure 1    Regional impacts of climate change on pesticide application [in percent]**
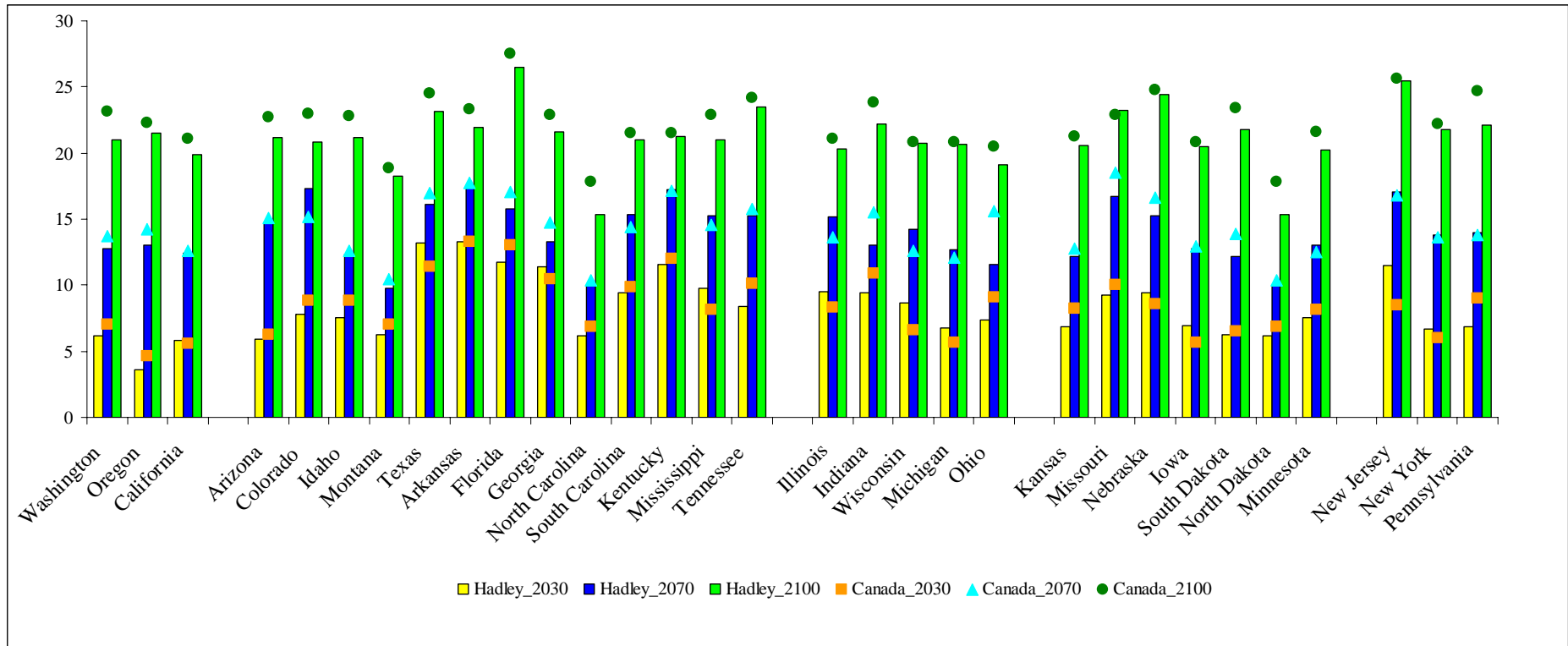
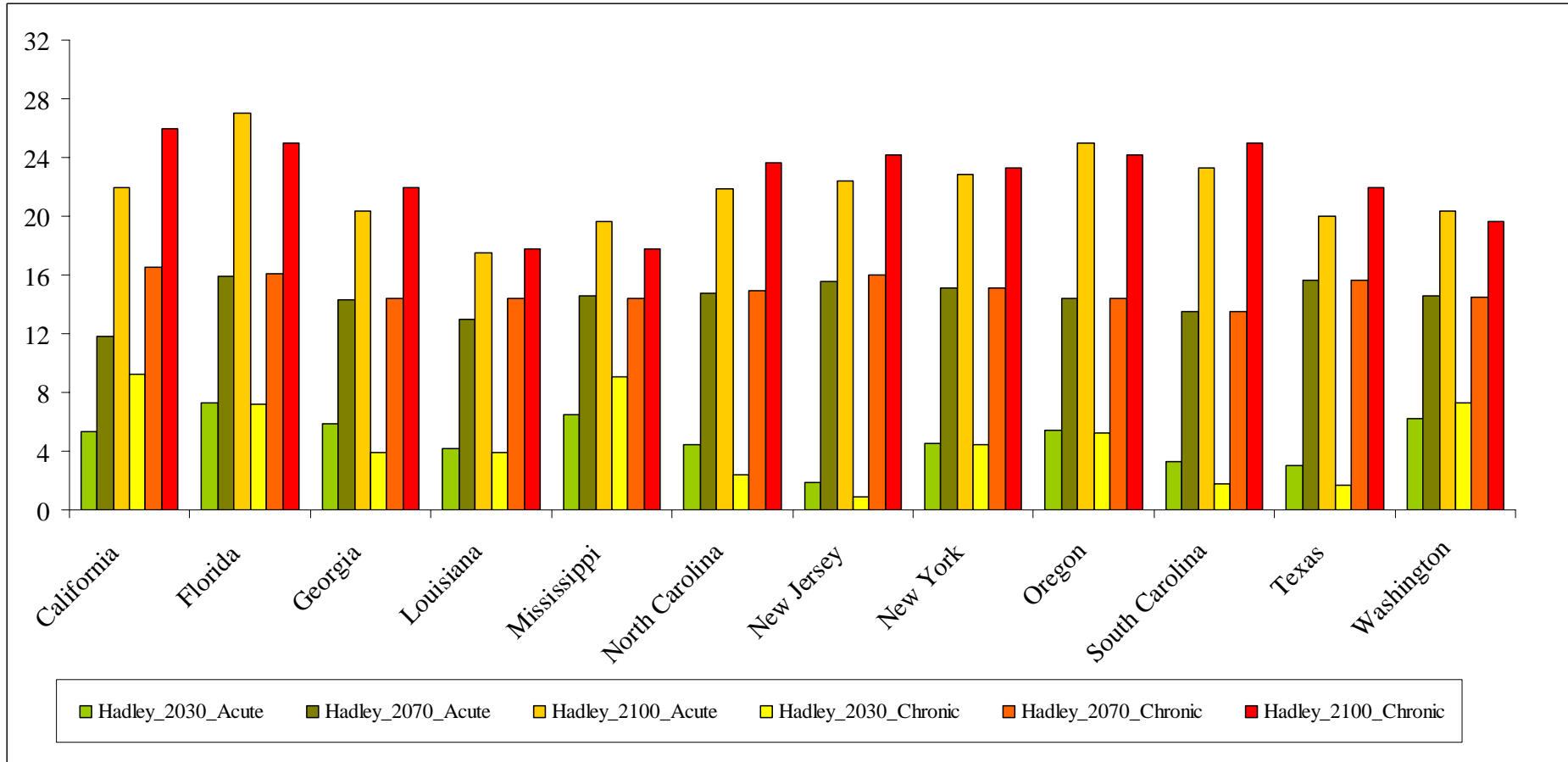**Figure 2    Impacts of climate change on the use of individual pesticide classes [in percent]**
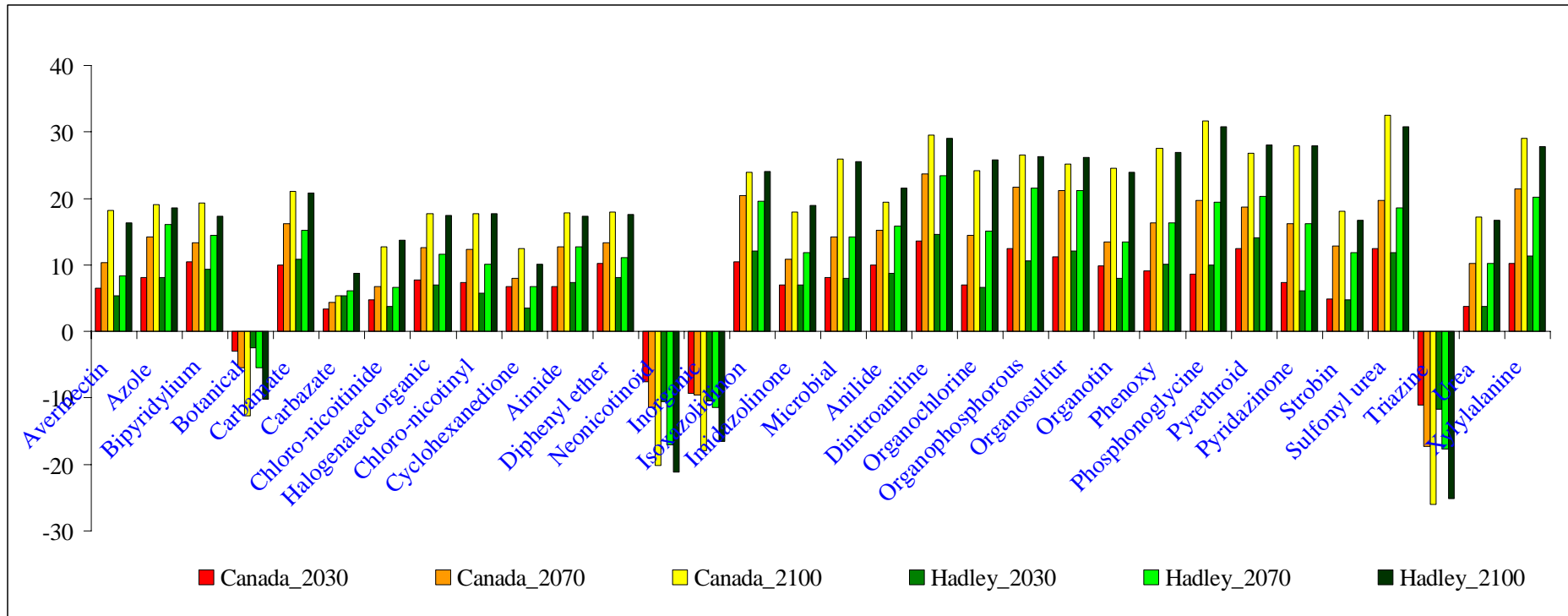
**Figure 3    Impacts of climate change on pesticide application to different crop types [in percent]**
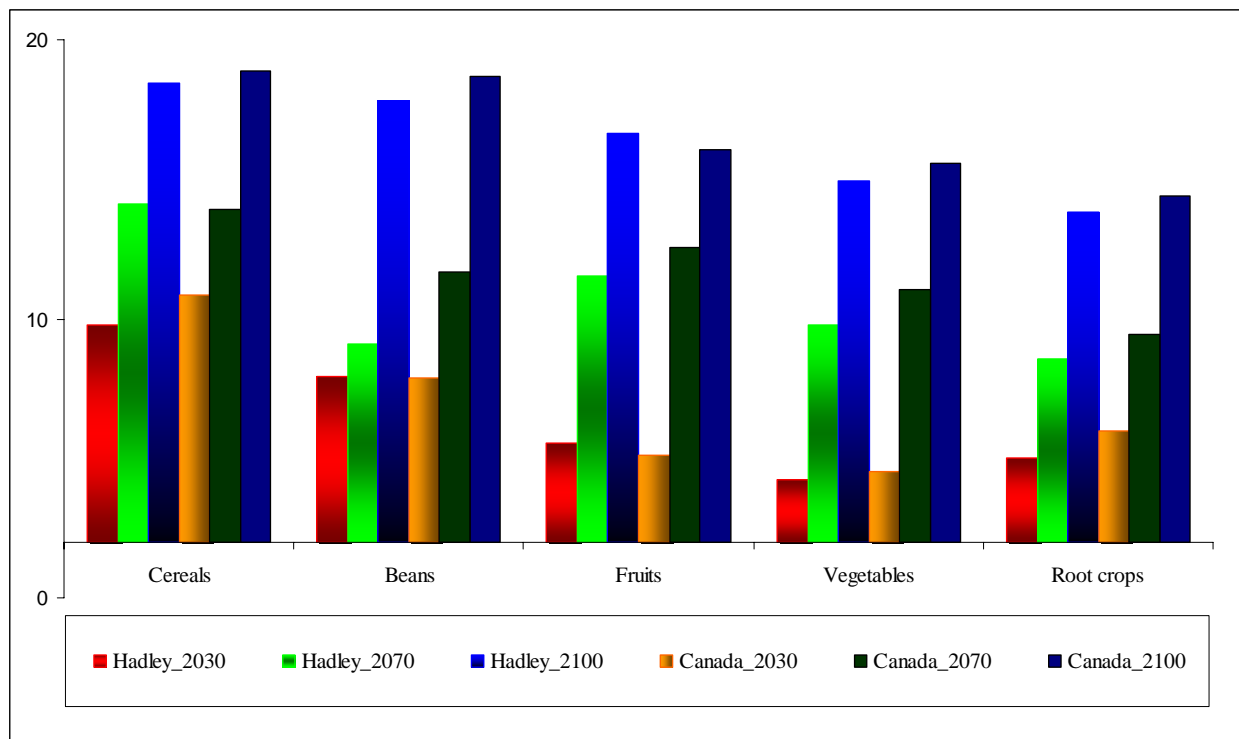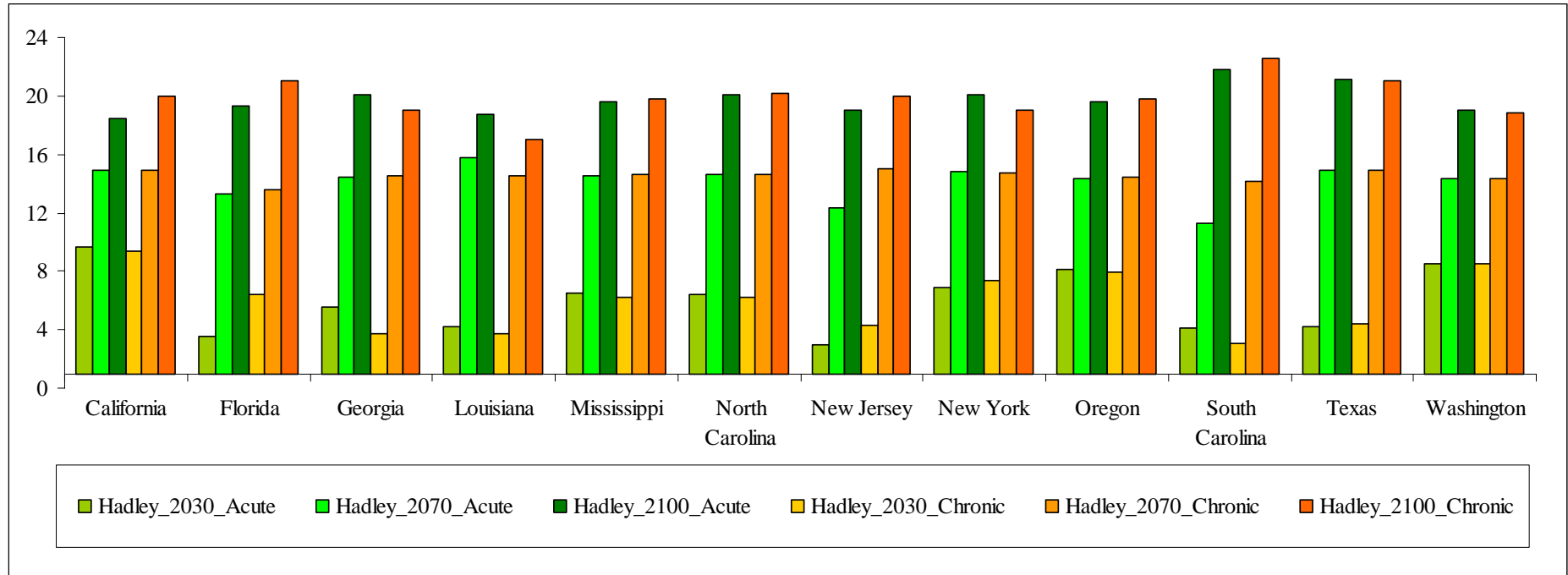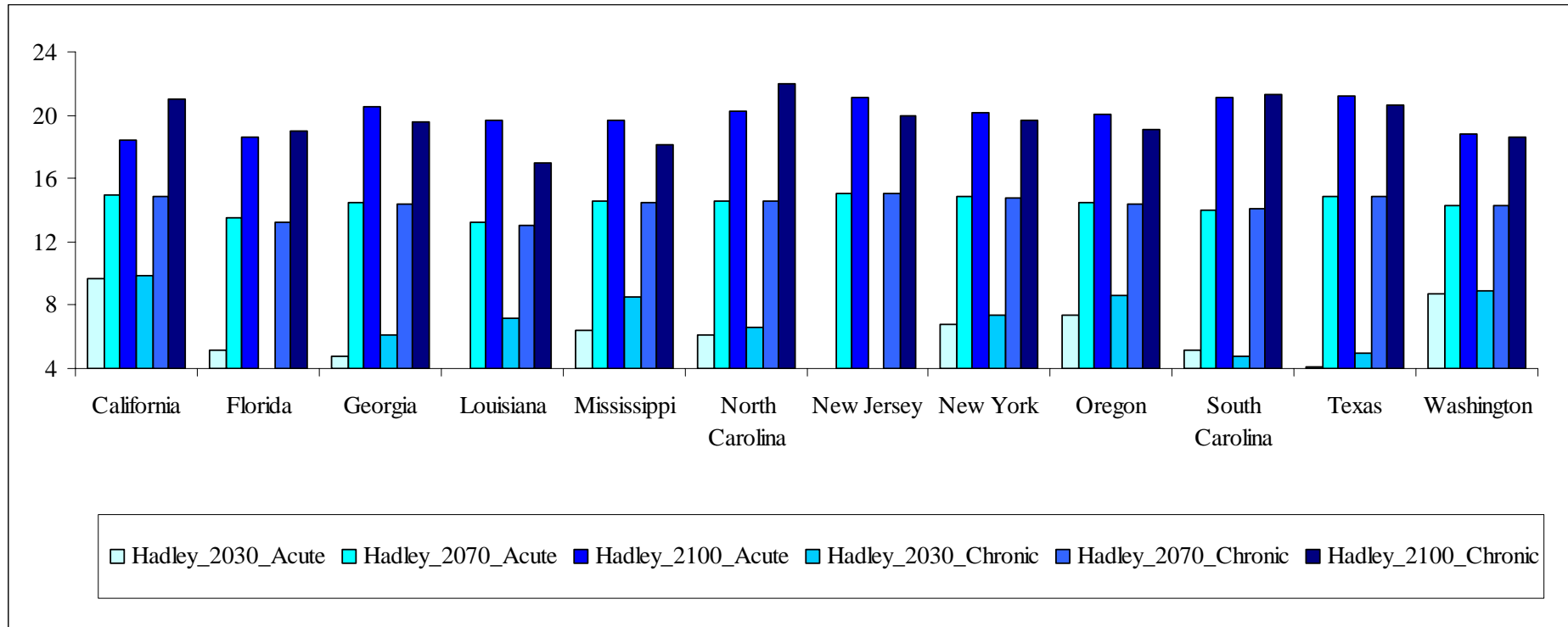
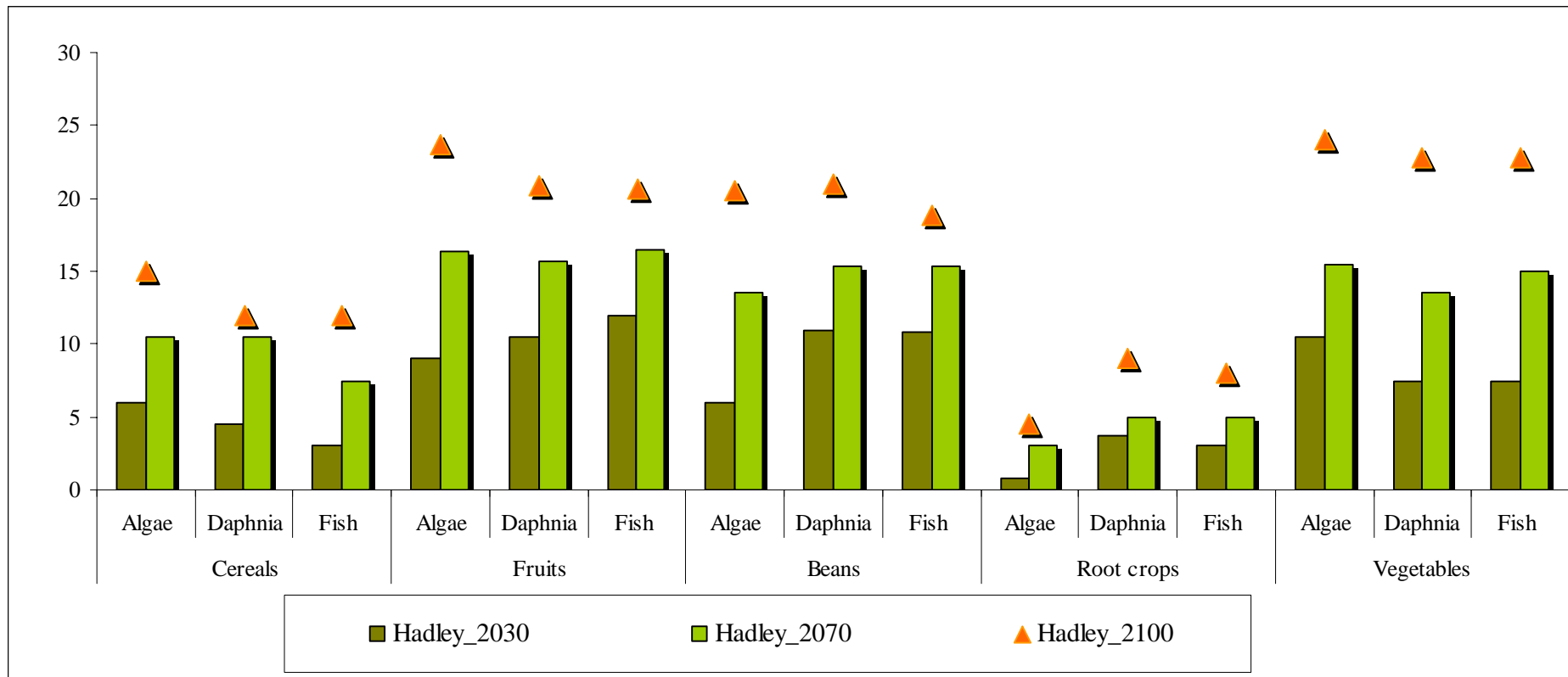**Figure 4    Impact of climate change on relative changes in toxicity risk for algae across US states [in percent]**

**Figure 5    Impact of climate change on relative changes in toxicity risk for daphnia across US states [in percent]**
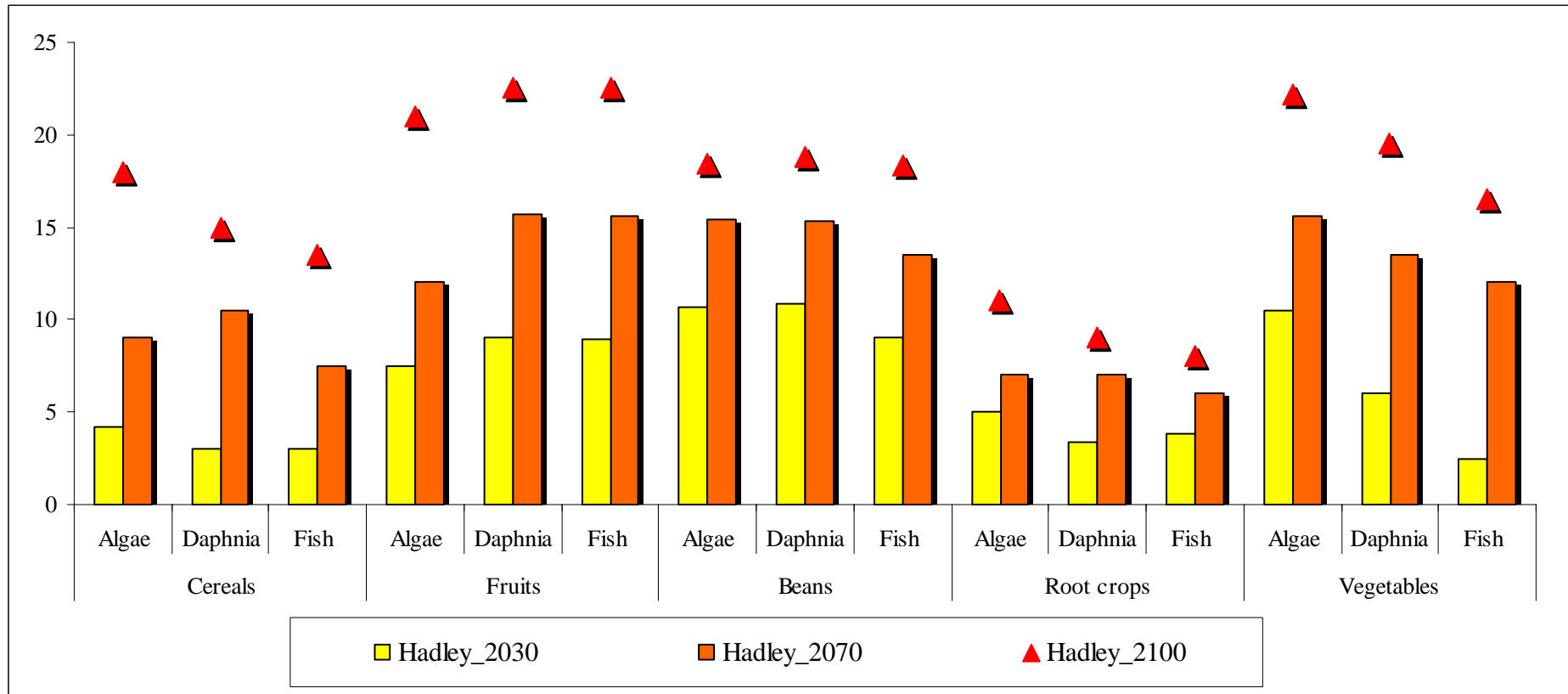
**Figure 6**    **Impact of climate change on relative changes in toxicity risk for fish across US states in [percent]**

**Figure 7    Impact of climate change on relative changes in acute toxicity risk for major crop types [in percent]**

**Figure 8    Impact of climate change on relative changes in chronic toxicity risk for major crop types [in percent]**

# Appendix 1    Structure of the Aquatic risk indicator REXTOX

In 2000, the OECD designed and developed several aquatic risk assessment tools for national authorities to monitor progress on measures designed to reduce the environmental risk of pesticides. The proposed indicators were ADSCOR, SYSCOR and REXTOX. They represent different combinations of mechanistic and scoring approaches and use information on pesticide application and environmental consequences at national or regional level. In all three indicators relative risk values are estimated by calculating the "exposure-toxicity ratio". While all indicators include toxicity to the same organisms (algae, daphnia, and fish), they differ in the approach of exposure estimation. Of the three alternatives, REXTOX uses a mechanistic approach and is the only indicator considering several field site properties. Thus, REXTOX resembles most closely risk assessment in its basic structure and concept.

REXTOX consists of three major equations blocks. The first block calculates losses which are defined as the amount of pesticides leaving agricultural fields via spray drift, run-off or lathing. The second block calculates exposure of pesticides in surface waters. The third part calculates the toxicity risk. More details on each of these blocks appear below.

Calculation of losses

Spray drift losses (Lsd), are calculated using parameters (equations 1-5) from a regression model (Ganzelmeier et al 1997). The terms of equations are**:** a and b **-** regression coefficients obtained from Ganzelmeier's tables (OECD, 2000*)*, and Width of water buffer zone (Wbz). By definition Wbz depends on the distance between the spray and the water bodies and the size of the water body (OECD, 2000*)*. As a condition for their legal permission and registration, some pesticides require the implementation of buffer zones to ensure the

adequate protection of the aquatic organisms. A stationary buffer distance (6 m from the water's edge or 5 m from the bank top) is required for most of the agricultural pesticides (EPA, USA 2006).

**Table A1 Model equations**

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**I. Losses**

$$\sum_{c}^{n} Lsd_{ics}\% = (a - b \times \ln(Wbz_{is}^{2})) \tag{1}$$

$$\sum_{c}^{m} Lsd_{ic}\% = \frac{1}{(a + (b \times Wbz_{ic}^{2}))} \tag{2}$$

$$\sum_{c}^{p} Lsd_{ic}\% = \left( a + \frac{b}{Wbz_{ic}^{2}} \right) \tag{3}$$

$$\sum_{c}^{q} Lsd_{ic}\% = EXP(a - b \times \ln(Wbz_{ic}) \tag{4}$$

$$Lsd_{ic}\% = \left(Lsdnbz_{ic}\%\right) \times \left(1 - Compliance_{SDB_{ic}}\right) + \left(Lsd_{ic}\%\right) \times \left(Compliance_{SDBic}\right) \tag{5}$$

$$Lro_{ics}\% = (Q_{s}/\Pr_{s}) \times Cr \times f1(Slope) \times f2(Run - off\_BZ) \times 100 \tag{6}$$

$$Lro_{ic}\% = \left(Lronbz_{ic}\%\right) \times \left(1 - Compliance_{RODB_{ic}}\right) + \left(Lro_{ic}\%\right) \times \left(Compliance_{ROBic}\right) \tag{7}$$

$$Cr = \exp\left( -3 \times \frac{\ln 2}{DT_{50}soil} \right) \times \left( \frac{1}{1 + \left( \dfrac{Koc \times \%OC}{100} \right)} \right) \times \left( \frac{1 - Pl\text{int}}{100} \right) \tag{8}$$

$$f1_{slope} = 0.02153 slope + 0.001423 slope^{2}; \tag{9}$$

$$f2_{BZ} = 0.83^{Wbz}; \tag{10}$$

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## II. Exposure

$$EX_{(i,c,s)} = Adr_{ics} \times \left( \frac{Lsd_{ics}\% + Lro_{ics}\%}{Wd_s} \right) \times Wi_s \times Nap_{ics} \times Bta_{ics} \qquad (11)$$

## III. Risk

$$REXTOX\,Scaled\_Acute_{(i,c,s,l)} = \frac{Ex_{(i,c,s)}}{Atox_{(i,l)}} \qquad (12)$$

$$REXTOXScaled\_Chronic_{(i,c,s,l)} = \frac{Ex_{(i,c,s)}}{Chrtox_{(i,l)}} \times LTF_{is} \qquad (13)$$

$$LTF_{is} = \frac{C_{is}}{Ci_{is}} = \frac{1 - e^{-\frac{\ln 2}{DT_{50}} \times 21}}{\frac{\ln 2}{DT_{50}} \times 21} \qquad (14)$$

| Sets | Subsets |
|---|---|
| *i* -pesticides | $m \in c$  early fruits |
| *c* – crops | $n \in c$ late fruits |
| *s*- region | $p \in c$ early arable |
| *l*- aquatic species category | $q \in c$ late arable |

**List of variables**

| | |
|---|---|
| Lsd  - Losses via spray; | Q- runoff volume drift; |
| Lro - Losses via run-off | Pr - precipitation; |
| Lsdnz- loses via spray drift without buffer | DT 50 soil – soil degradation; |
| Lronb*z* - losses via run off without buffer | Wbz -  water buffer zone; |

Koc- sorbcion coefficient of organic carbon  OC- organic carbon;

Plin*t*- plant interception  Wd- water depth;

Ex - exposure scaled;  Wi - water index

Nap – number of application;  *f1,f2*- slop of fields;

REXTOX Scaled_Acute- aqute risk;  *a,b*- regression coefficients;

REXTOX Scaled_Chronic-  Chronic risk;  Bta – basic treated area;

LTF- long-time factor;  Cr - Pesticides in soil surface;

Adr -dose rate applied by farmers;  C - concentration ;

The indexes m,n,p,q capture differences between crop cultivation types and pesticide application timing (Ganzelmeier et al. 1997). Following the original REXTOX model, management practices are linked to the stage of crop development. The equations are split between the early fruits m, and late fruits n, and between early arable crops p and late one q. The total amount of losses via spray drift is calculated in equation 5. The spray drift buffer compliance factor is incorporated by calculating Lsd(%) with and without buffer and putting the value in the equation 5. Losses via run-off are calculated in equation (6). By equation (6) the relative loss via run-off ($Lro_{ics}$%) is proportional to application dose rate available in run-off water as dissolved substances, Q – runoff volume (mm).  The run-off volume is obtained from tables based on models by Lutz (1984) and Maniak (1992), which cover two soil types (sandy, loamy) and three scenarios considering application time, crop and soil moisture: Scenario 1 application in autumn on bare soil with high soil moisture; Scenario 2 application in early spring on bare soil with low soil moisture; Scenario 3 application in early summer on

bare soil with low soil moisture; Depending of the soil type and scenario the corresponding run-off volume is picked up from the table for each value of precipitation between 1 and 100 mm. $Pr_s$ is the mean of daily precipitation (mm/day) during growing seasons. Rain events are assumed to occur 3 days following application of pesticides (OECD, 2000). Cr is the amount of pesticides relative to the dose applied available for runoff 3 days after application. The calculation of that amount of pesticides (Cr) is given by equation (8)

Within the first tree days the compound is depredate under first order kinetics (exp -3 x Ln2/ *DTsoil50).* DT 50 soil is half-life time (days) of active ingredient in soil. Only the contribution to the dissolved concentration in the water is considered.

{ (Koc x %OC)/100} is ratio of dissolved to sorbet pesticides concentrations with Koc - sorption coefficient of active ingredient to organic carbon and %OC organic carbon content in the soil.

Finally, the proportion of pesticides reaching the soil depends on the amount that is intercept by the plant ( *Pl*int) when it is applied {(1- *Pl*int) /100} ( equation 7).

Equation 8 show the correction factor for slopes of fields *(f1,f2).* Below 20 % losses via runoff increase following the formula (equation 9) and are it constant for the slops larger than 20 % up to 20 % f1 is set up to 1. The correction factor for the buffer zone is calculated with equation 10. The losses via runoff increase exponentially with the width of the buffer zone. If the buffer zone is not densely covered with the plants, the width is set to zero (0 m).

The total amount of losses via runoff is calculated similar to the total amount of losses via spray drift (equation 10). As is done for spray drift, runoff buffer compliance factor is

incorporate by calculating *Lro* % with and without buffer in the following formula (equation 10):

Calculation of Exposure

Exposure is calculated at tree levels. The levels can be used separately or as a complex which allows comparing risk in association with recommended and practice. The first level exposure is calculated based on the recommended dose rate or base on the maximum quantities of pesticides that are suggested to be applied.  The others two Exposures "*Unscaled*" and "*Scaled*" are based on the actual dose rate the quantities of pesticides applied by farmers. Exposure "Unscaled" represents the average of typical treatment on one average hectare in agricultural practice. Calculation is called "Unscaled" because it is done at the unit level rather than begin scaled up to a regional or national level. Exposure "Scaled" is the most extended of available use data. It is because is calculated to the national or regional level. Scaled Exposure calculation is given by equation 11. The terms of equation 11 as follows: Actual dose rate (*Adr)* of applied pesticides multiplied by sum of losses (from spry drift and runoff in percent) divided by water depth, Water index which stands for the proportion of agricultural area bordered by surface water bodies, number of application, and basic treated area which is the proportion between treated with pesticides area and total planted area.

Calculation of toxicity risk

The risk index is calculated as a proportion between exposures to toxicity ratio Equation (12,13).The terms of equation 13 are as follows: REXTOX_Acute is the acute risk index; Ex is the exposure and Atox is the laboratory value of LC 50 or lethal concentration or

concentration that have lethal effect on 50 % of the tested species ; $i$- is pesticide, $c$ is crop group, s is state, $l$ is aquatic species group.

Thereby, long-term risk is calculated on the same principal (equation 14) but exposure is multiplying with a so-called long term factor (equation 15). This factor indicates the ratio of the weighted average pesticide concentration (calculated on the basis of first-order degradation kinetics requiring DT50, water values) over a certain period (default value of 21 days was considered in correspondence to regular time period of long-term toxicity tests) and the initial concentration (OECD, 2000).

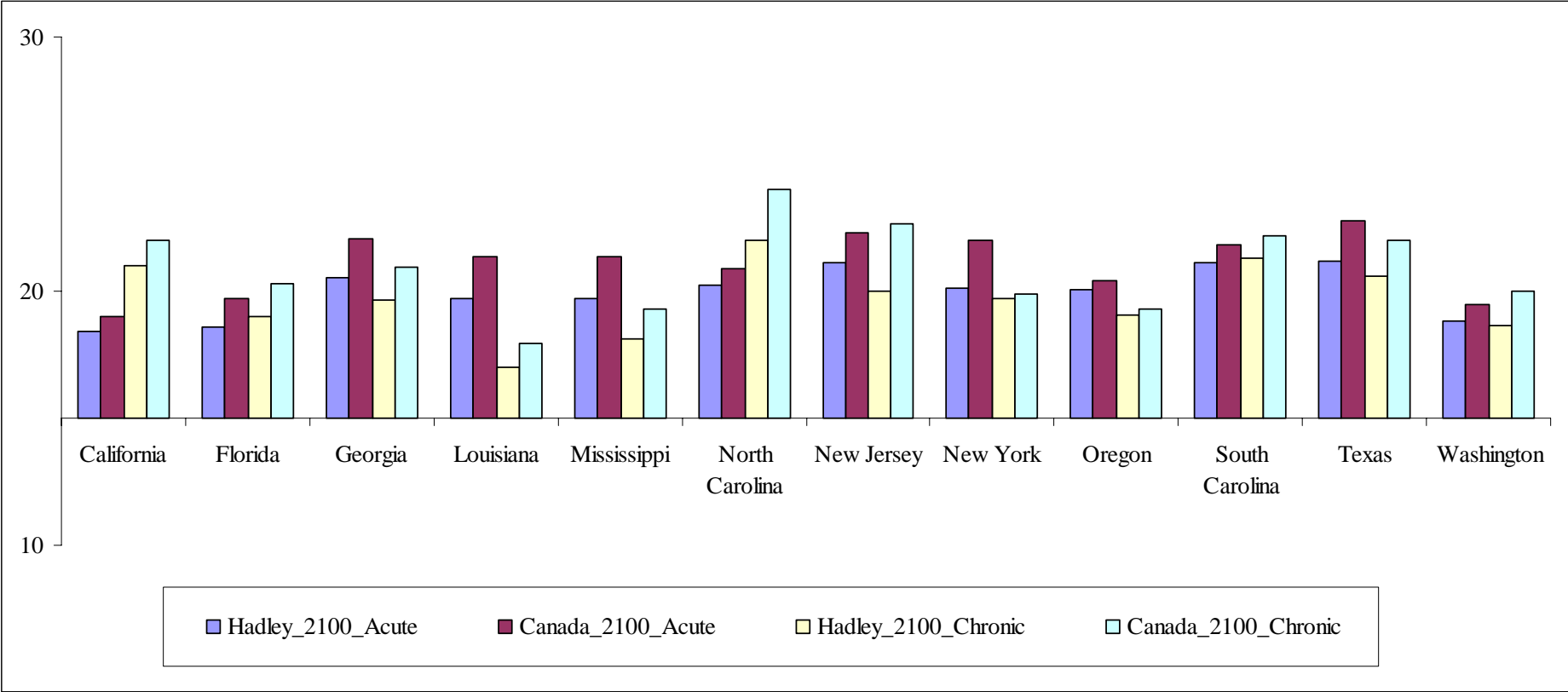# Appendix 2      Toxicity risk changes from pesticide adjustments to projected climate change in 2100

**Figure A2-1**      **Toxicity risk changes for algae**
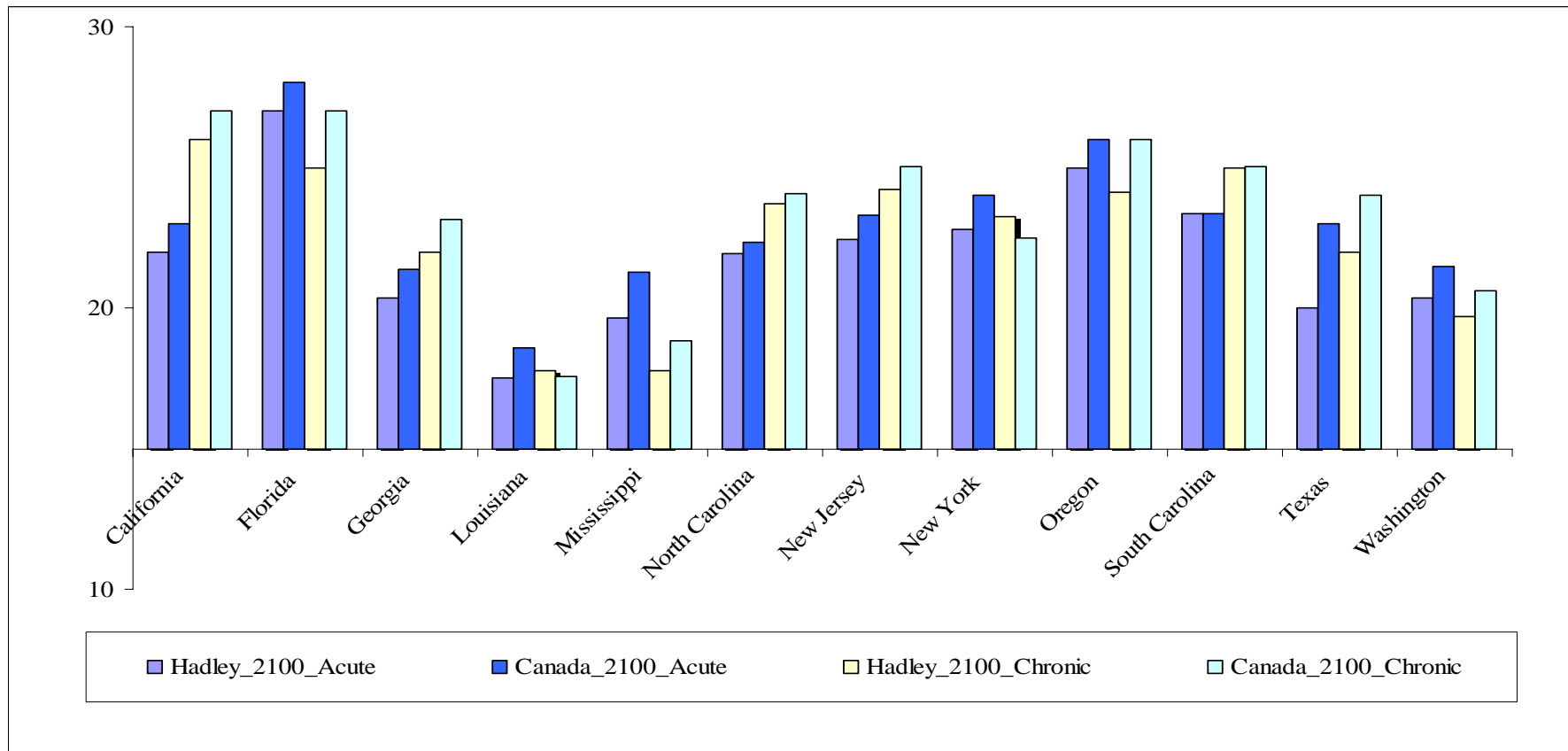
**Figure A2-2          Toxicity risk changes for daphnia**
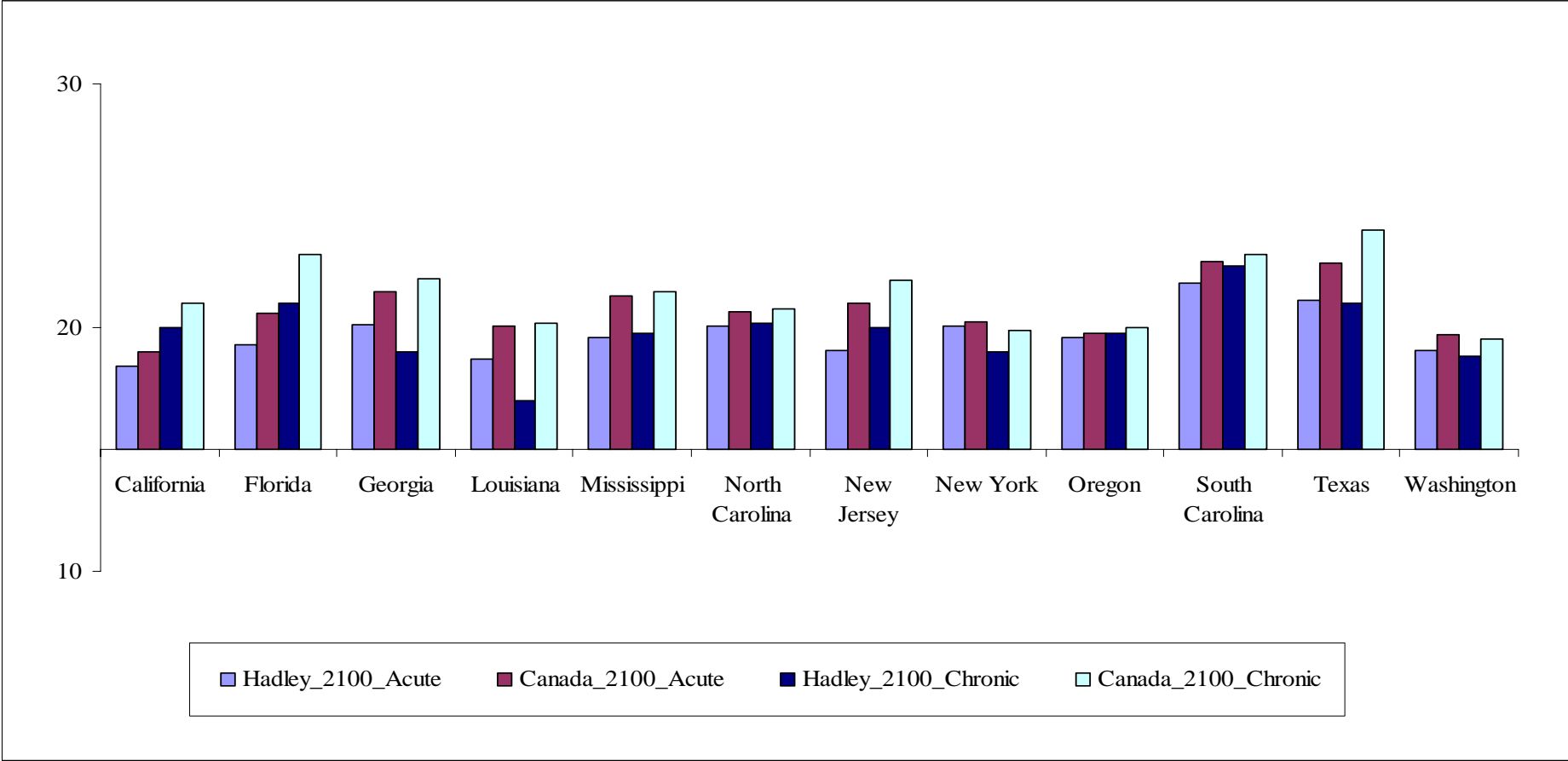
**Figure A2-3       Toxicity risk changes for fish**

## Appendix 3    List of pesticides which do not alter aquatic risk in response to climate change

| Acute toxicity risk | Chronic toxicity risk | Acute toxicity risk | Chronic toxicity risk | Acute toxicity risk | Chronic toxicity risk |
|---|---|---|---|---|---|
| Algae | | Daphnia | | Fish | |
| Bromoxynil | Dimethoat | Bentazon | Pendimethalin | Triadimefon | Oxydemeton |
| Cyfluthrin | Iprodione | TebuconAzole | Ethephon | Carfentrazone | Methamidophos |
| Fenoxaprop | Bromoxynil | FenbuconAzole | Bentazon | Bentazon | Diflubenzuron |
| Fluazifop | Fenoxaprop | Bromoxynil | Bromoxynil | Bromoxynil | Iprodione |
| Iprodione | MCPA | Cymoxanil | Fenoxaprop | Cymoxanil | Bentazon |
| MCPA | Oxydemeton | Ethephon | MCPA | Ethephon | Metiram |
| Oxydemeton | Propamocarb | Fenoxaprop | Propamocarb | Iprodione | Bromoxynil |
| Propamocarb | Rimsulfuron | MCPA | Rimsulfuron | MCPA | Ethephon |
| Thifensulfuron | Thifensulfuron | Propamocarb | Thifensulfuron | Propamocarb | MCPA |
| Tribenuron | Tribenuron | Thifensulfuron | Tribenuron | Thifensulfuron | Propamocarb |
| Metalaxyl | | | | Tribenuron | Thifensulfuron |
| Ethephon | | | | | |
| Cymoxanil | | | | | |