Review of the Ph.D. dissertation of Mgr. **David W. Hardekopf** entitled **"Modeling the recovery of anthropogenically acidified mountain waters"** submitted at Charles University in Prague

The dissertation consists of very short introduction and five medium-sized scientific papers already published in international reviewed journals. David Hardekopf is the first author only of the last paper recently published in the Hydrology and Earth System Sciences. Impact factor (IF) of this journal was 1.3 in 2006 according to the Web of Sciences (WOS). He is the second author of the paper Kopáček et al. (2006) published by the Journal of Limnology, which is excellent scientific journal but unfortunately not impacted by the WOS. David Hardekopf is the 3rd author of the paper Kopáček et al. 2006 published in Biologia (IF 0.2), the 4th author of the paper Horecký et al. 2006 published in Water, Air, and Soil Pollution (IF 1.2) and the 9th author of the paper Wright et al. 2006 published in the Science of the Total Environment (IF 2.4).

The dissertation focused on assessments of the stream benthic macroinvertebrates in heavily acidified Czech streams with major focus on one branch of the Litavka catchment, Brdy Mts. The rain-fed branch of the heavily acidic Litavka stream was assessed by the biogeochemical model MAGIC. Several scenarios of future development of the streamwater and soil chemistry with respect of the Gothenburg Protocol scenario of atmospheric deposition and also predicted climatic changes were simulated. Moreover these predictions were compared with the possible future status of the benthic macroinvertebrates at headwaters of the Litavka catchment. The dissertation also evaluates with great detail chemical recovery of large amount of lakes in the Tatra Mountains and predicts theirs future chemical recovery by application of the MAGIC model. The main body of the dissertation is supported by the modeling of climatic change effects on streamwater chemistry in numerous European catchments.

All parts of the dissertation have exceptionally high scientific level and the results are at least of European importance. David Hardekopf played very active role in difficult and interdisciplinary research in cooperation with top Czech, Slovak and foreign scientists. Therefore my conclusion about the dissertation of David Hardekopf is highly positive. He

sufficiently demonstrated high scientific level of limnological field work, data processing and evaluation, geochemical modeling and writing skills for top scientific journals.

I hope that his scientific career will successfully continue after the Ph.D. defense.

However I have some minor criticism of some parts of the dissertation. More important questions are bold. My comments follow:

1) Introduction to the anthropogenic acidification (pg. 3) could perhaps include some important papers from the Hubbard Brook Experimental Forest watersheds, NH, USA (e.g. Likens et al.).
2) **The author wrote (pg. 3) that "acidification in Czechoslovakia… was first recognized….by Fott, Stuchlík and Stuchlíková, 1987"). The cited paper (published in the GEOMON conference proceedings) has been definitely important however some older Czech acidification research published in prestigious journals was omitted (e.g. Pačes T., 1985. Sources of acidification in Central Europe estimated from elemental budgets in small basins. Nature 315: 31-36).**
3) Pg. 4. Sulphur (not Sulpher).
4) Note the reference Veselý et al., 2002 (pg. 4) is only about streamwater in selected Czech mountains, not about Slovak lakes.
5) The reference Keller et al., 2002 (pg. 5) is missing in the list of references (or the year is wrong: Keller et al., 2007 in the list of references).
6) **Pg. 6. The statement "acidification models …. are based on the same principles …." is a gross oversimplification. For example the SAFE model (Warfvinge et al. 1993, Environmental Pollution 80: 209-221) calculates implicitly chemical weathering from the mineralogical composition and grain size of soils. On the other hand only the newest versions of the SAFE model calculate simple sulfate sorption is soils (Martinson et al. 2003, Environmental Pollution 124: 119-125). The PnET-BGC model (Gbondo-Tugbawa et al. 2001, Water Resources Research 35: 1057-1070, Gbondo-Tugbawa et al. 2002, Ecological Application 12: 8-23, e.g. Figure 3, page 13) calculates not only sulfate sorption like the MAGIC but also sulfur mineralization of organically bound soil sulfur. All these examples show that the models mentioned in the reference of Tiktak and van Grinsven do not have only the same or similar principles like the MAGIC model used in the evaluated dissertation. Moreover even the MAGIC model (Cosby et al. 1985-2001) developed significantly in its complexity especially by the inclusion of organic acids dissociation in the version 5 and soil nitrogen processes in the version 7.**
7) Typing error on pg. 7 (…driven by levels of…) (not…. "my"….)

   Paper of Horecký et al. 2005 WASP:
8) **Pg. 13. Could you describe how the streamwater flow was measured in the field?**
9) Pg. 13. It would be better to use more detailed maps 1:10,000 instead of 1:50,000 for the measurements of the stream length ("distance from source").

   Paper of Kopáček et al. 2006 Biol.:

10) Pg. 29. Many researchers (especially from Scandinavia) think that chloride in atmospheric deposition is derived only from the ocean spray, however you have cited opinions that significant portion of chloride was associated with industrial emissions of HCl in the Czech and Slovak Republics. Are the real measurements of industrial emissions of chlorine in the Czech Republic available?

11) Pg. 32. Prechtel (not Prechetel).

Paper of Kopáček et al. 2004 JL:

12) Pg. 40 (Tab. 2). What was the valence of aluminum?

13) Pg. 41. The MAGIC model is technically calibrated to one year. Which year(s) was (were) used for the modeled lakes?

14) Pg. 42. Measured soil sulfate adsorption capacity was lower than the calibrated value used in the MAGIC modeling. Could you hypothesize about reasons for that discrepancy? What are potential consequences for the long-term predictions of sulfate concentrations in surface water?

15) Pg. 43. What kind of S-bearing minerals in bedrocks would you expect at that site?

16) Pg. 47-49. The Satanie and Starolesnianské Lakes are in the extremely sensitive lake category. Which lake was situated as the third one in that lake category?

Paper of Wright et al. 2006 STE:

17) Pg. 55. Birkenes catchment is also a part of the ICP Integrated Monitoring program.

18) Pg. 56. Is the vegetation information about the Čertovo Lake correct ("mixed deciduous-coniferous forest")?

19) Pg. 64. The references of Kopáček et al. 2003a, 2003b are exactly the same.

20) Pg. 64. Bohemian Forest (not "forest").

Paper of Hardekopf et al. 2008 HESS:

21) Pg. 67. Exactly same comment like in 2)

22) Pg. 67. The Gothenburg Protocol is not part of the "European Union" agreements. What is the meaning of the cited abbreviation: UN-ECE?

23) Pg. 69 and Fig. 3 (pg. 72). Sampling in the past was highly variable with respect of the time scale:
November 1998 – March 2000 22 samples, 2001 27 samples
2000 2 samples, 2003 0 samples, 2004 2 samples, 2005 5 times, 2006 1 sample
In my opinion the best approach for most streams would be to use the discharge-weighted annual means for comparison to the MAGIC model output. **How the discharge-weighted annual mean compares with the arithmetic mean at Litavka (e.g. for the solutes in Fig. 3)? I am aware that detailed comparison could be done perhaps only for 2007 when the new advanced device for continuous runoff monitoring was installed. I am aware that the year of 2007 is not part of the published paper.**

24) Pg. 481, Tab. 69. Is the weathering = 0 of sodium in the MAGIC model reasonable? It looks like no minerals of sodium are available in the catchment.

25) **Pg. 481, Tab. 69. Is the uptake > 0 of sodium in the model reasonable? According to fairly old German concepts (Ulrich et al., later in Bredemeier 1988, Water, Air, and Soil Pollution 40: 121-**

138) sodium is not part of the internal biological cycling in trees. Consequently sodium is frequently used for calculations of dry deposition factor of other three base cations.

26) Pg. 69. Soil chemistry and stream water chemistry for a reference year are not inputs to the MAGIC model. I suppose the model just calculates them.

27) Pg. 70, Fig. 2. Predicted increase of average air temperature is 3.7^{o}C. How can such warming increase the evapotranspiration (mm year^{-1}) in forest ecosystems in general. Consequently should we expect lower annual streamwater runoff (mm year^{-1}) and water shortages in the growing season?

28) Pg. 70, 3. Weighting of throughfall and bulk precipitation fluxes for the calculations of the total deposition. For which compounds was the weighting used in your assessments?

29) Pg. 71. The predicted 4^{o}C increase in temperature was incorporated to the MAGIC by estimating changes in chemical weathering, release of organic carbon, soil nitrogen mineralization and uptake by trees. No significant changes in precipitation were predicted (and the annual mean streamwater runoff was left intact in the MAGIC model). Potential decrease of streamwater annual runoff due to warming and consequent evapotranspiration increase was not considered in the published model simulations. Could it be important at Litavka?

30) Pg. 72. 4.1. Typing error. Redundant one "in".

31) Pg. 74. Modeled soil pH 4.2. I think it should be soil water pH. In my opinion the MAGIC model does not calculate soil pH. Do you agree?

32) Pg. 80. Keller 2007 or 2002? Ad comment 5).

33) Pg. 81. Sulfur (not Sulfer).

34) Pg. 81. Delete "figs. Berlin, Heidelberg, Tokyo 1986" in the end of the reference.

35) van Grinsven (not Vangrinsven).

36) Split two references (UNECE 1999 and UNECE 2004).

37) Rogora (not Rogera).

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in Prague, June12, 2008

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