**Hydrology and
Earth System
Sciences
Discussions**

Interactive
Comment

Interactive comment on "The influence of heterogeneous groundwater discharge on thetimescales of contaminant mass flux from streambed sediments – fieldevidence and long-term predictions[1]" *by* C. Schmidt et al.

Anonymous Referee #2

Received and published: 23 May 2008

General comments: The paper presents two fundamental findings: (1) Concentrations of contaminants in a streambed are qualitatively inversely correlated to previously measured groundwater fluxes; and (2) the timescale needed for concentration to reduce by 90% is at least decades and probably much longer in most cases.

The concept of the work is useful at filling in how contaminants are distributed and how they may decrease over time in streambed sediments. It builds on a nice earlier study

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[1]Invited contribution by C. Schmidt, one of the Union Young Scientist Award winners 2007.

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that estimated groundwater fluxes in the same stream.

My major concern with the paper is that it has an incomplete view of sorption. If this work were presented to me by a consultant in my community, I would be very concerned that the cleanup times mentioned would not be reasonable because of inadequate assumptions on sorption. I would ask the consultant to fill in more of the details on the sorption story. I find myself needing to suggest the same thing here, because consultants or government agencies will tend to look at this kind of work and say that this is the state-of-the-art, and use it to defend inadequate work.

The paper assumes linear, equilibrium sorption. However, there is insufficient evidence that either assumption is valid. While an isotherm appears to have been measured, the isotherm is not presented, so I have no way of knowing if the isotherm is linear. Therefore, the first thing the authors must do is present the sorption data upon which the rest of their work is based.

Secondly, the paper assumes equilibrium sorption. The data that support this are shown in Fig. 3. However, if I understand the data correctly, these are sorbed fraction concentrations. In all cases, the sorbed fraction appears to rise at early time. In some cases it drops and then rises again. I assume, possibly incorrectly, that different aliquots were used for each data point, suggesting that the inter-sample variability is greater than the desorption signal. In any case, rising concentrations in the sorbed fraction during a desorption experiment does not make sense, and suggests a serious methodology issue. Therefore, the authors probably cannot claim to know that sorption is at equilibrium over the timescales of transport in the problem.

It is unfortunate, but these two issues make the paper difficult to recommend at this point. I like the overall concept of the work, but the conclusions are currently based on faulty sorption assumptions. Since the main novel contribution of the paper is the timescale of contaminant release, this is a very serious problem.

Specific comments by line #:

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Interactive Discussion

Discussion Paper

p 972 - 12 the flow rates are not results from this paper, and should be clearly marked as such. Alternatively, the methods used to derive these GW fluxes should be clearly outlined in the paper (which I would imagine would make the paper redundant with the 2006 paper). - 22 The method you used to estimate reduction time to 10% mass should be a minimum time estimate. Time could be greater due to nonlinear sorption or kinetics. This needs to be stated.

p 980 - 16 Finite difference schemes have numerical dispersion, so in fact, you do have dispersion in your model. Consequently, in fact, you modeled advection-dispersion. The numerical dispersion can be calculated. For example, see p. 158-160 of Zheng and Bennett, 1995. Some codes use numerical dispersion to simulate all dispersion, thereby modeling dispersion exactly.

p 978 - 22 What are the sediments? Mineralogy, grain size, and where did it come from (so we know how representative the samples are of stream bed sediments)? What is the organic carbon content? These are important for sorption characterization. How do we know if 48 h was enough?

p 978, 985 - please show sorption isotherm in a figure. This is very important, because the reliability of your conclusions depends on the quality of these data, and whether the isotherms are linear. The remediation time could be highly sensitive to this. For example, see Jaekel (1996).

p 984 - 3 – The conclusion about initial homogeneity does not seem well founded. It is based on assumptions and not data. Furthermore, all of the transport processes that the paper investigates would have been operating during 25 years of (probably time-varying) contaminant deposition.

p 987 - 6 the correct way to compare advection and diffusion timescales is with the Peclet number (which is precisely the ratio of the two timescales). Assuming $v = 0.036$ md-1, $D = 3 \times 10-10$ m2/s, and $L = 0.1$ m, the Peclet # is more than 100. Retardation factors go in the numerator ($v R$) and denominator ($D R$), so cancel each other. That

means that at 10 cm depth, advection is still by far the dominant mechanism of transport. This diffusivity (3 x 10-10 m2/s) is probably reasonable or maybe even high for the pore diffusivity for these compounds, because D should be lower than aqueous diffusivity because of tortuosity. Anyway, you should run through this calculation for various depths for this discussion. - somewhere in the discussion of results, the contaminant fluxes calculated from the stream bed should be compared to those observed in the stream. When I did the calculation, it appears that only about 2% of the contaminant flux in the stream can come from this reach based on the information given. Is this correct? (Avg. streambed discharge = 58.2 L/m2/d; streambed area = 660 m2; contaminant concentrations ~ 30 ug/L; therefore the mass flux is 13 ug/s; stream discharge = 200 L/s; therefore stream concentrations are 0.068 ug/L. However, you report stream concentrations much higher.)

Technical comments, by line #:

p 972 - 2-5 Recommend rephrasing sentence as follows. A small man-made near Bitterfeld, Germany was used by the chemical industry for waste water discharge until the early 1990s. - 6 is resulting from... results from - 18 run.... should be ran p 976 - 7 I do not think autochtone is an English word, but I could be wrong. Do you mean allochthonous? - 7 fluviatile should be alluvial p 977 - 11-12 phrase presumed to be capable to capture representative aqueous concentrations... needs to be preceded by a modal auxiliary verb parallel to can. More importantly, this phrase needs a reference - what work suggests that this is a reasonable presumption? - 29 You should very briefly review some of the most important findings of the Schmidt et al. paper. Did that paper find that there is no hyporheic exchange in the reach, since the model assumes only upward vertical groundwater flow? What is the hydraulic conductivity of the material? What is the vertical gradient? p 978 - 27 Place a comma after contaminant. p 981 - 6 what is the r2 and what are the confidence bounds on concentration comparing passive vs. snapshot concentrations? This confidence bound would feed forward into an uncertainty in estimates of time to reduce concentrations to 10% - 16 I think this

should refer to one or two specific samples, not the entire set. As the sentence reads now, it implies a problem with all of the samples. p 984 - 1-2 (and previous page) - this is redundant information, already given earlier p 987 - 19 was should be were p 988 - 12 analogue should be analogous - 18 has should be have p 989 - 11 this is the first mention of the organic content of the material. It needs to be measured and reported - it is very important to the Kd.

Fig. 4 the print in this figure will be hard to see - it needs to be larger.

References Jaekel, U., A. Georgescu, and H. Vereecken, Asymptotic analysis of nonlinear equilibrium solute transport in porous media, Water Resources Research, 32 (10), 3093-3098, 1996. Zheng, C., and G. D. Bennett, Applied contaminant transport modeling, Van Nostrand Reinhold, New York, 1st ed., 440 p.,1995.

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