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Interactive comment on "Improving the Accuracy of Model-based Quantitative NMR" *by* Yevgen Matviychuk et al.

Anonymous Referee #1

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The manuscript describes an alternative optimization routine (aka model adjustment procedure) to improve the accuracy of the model-based qNMR. The problem with existing frequency domain analysis is well described and the method proposed seems to certainly improve existing frequency domain methodology (GSD and its variants).

I wonder if they have suggestion and/or examples of such improvements with the existing time-domain modeling approach. While they eluded to such potential improvement in the introduction section for time-domain approach as well, there are no results to back that. I have particularly two concerns.

1. Fundamentally the Bayesian approach of Bretthorst (which is the engine behind the CRAFT method) does not fit each resonance to one given model (typically exponentially decaying sinusoid). Rather it fits the supplied time-domain signal (FID or digitally

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filtered subFID) to as many exponential decay models as needed to completely define it. I completely agree that a resonance (as per the NMR definition), more often than not, is non-Lorentzian in shape (for various reasons as pointed out by the authors). Attempting to fit that with a single model type (Lorentzian or gaussian or whatever the fancy maybe) will almost certainly bound to leave behind some part of the signa. The iterative approach of Bayesian approach defines such a resonance with "as many exponential models" as needed (again, more often than not) to completely define it (of course, within the limits of the residual noise and the probability function). The CRAFT approach, in particular, does not equate (or approximate) one resonance to one "best" exponential model, but rather as a complex sum of all the exponential models within a "segment width" (defined and introduced in the reference MRC 51, 821 and used in other subsequent reports) that defines the resonance (aka fingerprint). Such "segment definition" is best done as post data-decimation rather than as a constraint to it. CRAFT approach, hence, circumvents the such potential non-Lorentzian modeling by multi-exponential sinusoidal decay function. In other words, conceptually a resonance is not defined by the "best singular" model but rather by as many models needed to define it completely. 2. In time-domain method-optimization using residual spectrum (FT of the residual FID) as can be misleading – particularly when dispersive residuals are used as a guide to the efficiency of amplitude estimation. Majority of the cases (in time-domain analysis) the dispersive residuals are the result of error in frequency estimation. For example, for a resonance of 1 Hz linewidth an error in frequency estimation by 0.02% (100 Hz vs 100.02 Hz - in chemical shift scale on a nominal 400-500 MHz spectrometer, this is an error of 20 ppt – parts per trillion!) leads to recognizable dispersive residual in the spectrum – visualized after FT of the residual FID. Considering frequency and amplitude are orthogonal parameters in defining the NMR signal, improvement attempts to correct for such small error in frequency estimation to achieve "perfect" amplitude may be an exercise of academic interest.

I do agree with the authors and their methodology in improving qNMR estimation by frequency domain modeling approach. But it would be appropriate to put a note of

caution that such expectations of improvements are yet to be realized for time-domain methods. Alternately, I will like to see some results if similar improvements are to be extrapolated to time-domain modeling approach. Else, it could be prematurely misleading.

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