Dear Prof. Dharmawardena,

CDW: Thank you for the discussion and the tables. I have given my comments in RED to the more salient issues. I will put this up as your FINAL SAY for this round of discussions.

But we can discuss these in the future more directly between us by email]

As you have quite clearly admitted in your email 15/12/21 that you are not competent in the field of enzyme-substrate complexes, which are the key elements of the field of biochemistry, we are unable to accept your scientific reasoning in the discourse that we exchanged.

CDW: I stated that I do not agree to peer review articles that are not directly on topics that I am working on., because I will have to down load a lot of relevant articles etc., and then it takes too much of my time; also there is a responsibility to review the paper in about three weeks.

Nevertheless, your views and your paper provided the basis to reexamine the publications on CKDu and enable me to present the dangers of chelated heavy metals entering the food chains directly from inorganic fertilizers.

Biochemistry is the link subject of microbiology, soil sciences, plant sciences, human health, biology, zoology, ecology and other influencing subjects of chemistry and physics (thermodynamics). Therefore, mathematical expressions governing and linking them are the basis of evaluating ecosystems, biomes, and microbiomes. I was under the impression that everyone or most of us are competent to evaluate publications related to inorganic and organic fertilizers.

CDW: You have worked on non-equilibrium processes and know some of the mathematics, but would you agree to peer-review any of my articles on those topics, based on the claim that the science is the same?

I review inorganic fertilizers. We have also reviewed the CABJ publication on BFBF, i.e., *organic fertilizers* in this discussion because it is a straight comparison of harvests, and involves no microbiology. But I would not agree to review a paper containing only microbial processes as an anonymous referee. Because there are certain principles we must respect.

CDW: I am certainly able to understand all the mathematics, but as I said I don't peer review in a field where I have not published because it is not fair by the authors of that paper and I will have to accumulate all the references etc. and go through them critically and do everything in three weeks. Too much stress for a retired scientist doing many subjects from lasers to fertilizers.

Let me then walk you through salient aspects that I presented to this intellectual debate. Dr. Panabokke's findings on the formation of sesquioxide's of phosphorus are important to comprehend the poor quality of tropical soils. Thus, the vast quantities of existing phosphorous in the soil are not available to the plants. P is the primary element for transporting chemical energy to the plant.

CDW: Thanks. I had many discussions with Dr. Panabokke himself on all that. In fact in a paper I wrote jointly with Panabokke, we proposed two mechanisms for CKDu. One was macro-agrochemicals (not heavy metals) coming down from the hills along rivers like the Mahaweli and arriving in the dry zone

The other was the behavior of pits in cyclically dissolving and precipitating electrolytes during the dry to wet seasons (as may be in fact be occurring in stagnant water wells or regolith aquifers in the dry zone). I think the second mechanism, modified to be based on magnesium and fluoride ions has turned out have a lot of experimental support.

See the following link to the Cornell University registry, which is easier to download than from the journal

Article published jointly with Panabokke.

https://arxiv.org/pdf/1704.07906.pdf

In the absence of natural ecosystems for unlocking phosphate by increasing CEC from OM, inorganic fertilizers of NPK were used to provide macronutrients to the plant. SOC depletes with the application of inorganic fertilizers (Prof. Kulasooriya explained clearly and there are much research evidence) (FAO, 2017, https://phys.org/news/2021-12-nitrogen-impact-soil-carbon-sequestration.html)

When biochar is added to soil, it increases the CEC of soil on the condition that there is adequate SOC with stable OM. The organic carbon supplies the energy needed for the activation to transfer from ADP to ATP. Once chemical energy is available, the enzyme urease is not only able to catalyze the hydrolysis of urea, but because of their very high activity, free-living microorganisms can fix atmospheric nitrogen at normal temperature and pressure. It forms once again urea and or amino acids. N is the key element in enzymes (proteins). Now that it is clear how P and N cycles are functioning (receptor, as explained in email 6), it is important to define the role of K. K^+ is associated with various plant functions, emphasizing plant-mediated responses to environmental abiotic and biotic shifts and stresses by controlling transmembrane potentials and water, nutrient, and metabolite transport. Organic and mineral K like furnace ash, are in abundance in Sri Lanka for organic fertilizer productions.

Whenever logistic growth equation (LGE) is used for any biochemical transformations, both growth (alpha) and retardation (beta) coefficients should be used. Many are using K and a, without defining those terms. Prof. Tennakone should apply LGE only for the grain harvests. An increase in *α* (coef), given in

, will reduce yields because R is the second differential of N (we have publications of LGE used in leachate treatment and harvests). The tendency is to increase K and reduce *α* (coef), when inorganic fertilizers are applied. Inevitably preference is given to the uptake of HM. Unfortunately, paddy has an affinity for the uptake of HM and the plant breeders knew very little of the biomathematical relationships between nitrogen uptake and heavy metals (HM). The genetically modified rice is less in Fe and Zn. Cd for example will replace Fe or Zn in paddy grain, thus increasing yields because the growth coefficient increases with increased molar mass. It is noteworthy that K is a “squared” term. On the other hand, microbial activity is hampered by increased concentration of heavy metals, thus increasing *α* (coef) in their population growth following LGE.

CDW:The increased concentration of heavy metals that arises from inorganic fertilizer addition is only parts per trillion even after a century of application of even the worst mineral fertilizers.

Therefore, in the absence of bioaccumulation of heavy metals present in the microbes, the plant uptakes directly. Moreover, HMs are chelated. We must thank Prof. Tennakone for his contribution to our academic discussion.

We can also apply this to the bioaccumulation of heavy metals causing an increase in weight gain in humans. When HMs are replacing Zn for example, insulin resistance occurs causing T2D. Instead of LGE, Extension to MM kinetics can be used to determine inhibitions that can be compared with many factors and cofactors of enzymes, substrates, enzyme-substrate complexes, and their differentials, plus rates of reactions of the plant uptake, comparison with environmental factors, pH, etc. LGE has many mathematical weaknesses compared to EMM.

CDW; Note that Zn prevents the toxicity of cadmium by humans and other organisms. For references, see my article on cadmium in fertilizers, soils and food, *in Env. Geochemistry and Health*, 2018

Let us now examine the grain. The mineral content of rough rice will take away from the paddy cultivation approximately 5.2 % of the total harvest on condition that we return all the biomass, including paddy husk for the next season. The stable organic materials (OM) content needed each season will amount to 370 – 370 kg/ha, which should include, P, K, Ca, Mg, Zn, Fe, etc. The nitrogen is obtained from free-living microorganisms as explained above and from atmospheric lightning events.

In reply to Prof. Dhanapala, the values he has given for phosphate of 30-40 mg/kg and 30-40mg/50 kg could be for the US or European market. Please visithttps://wsrw.org/en/a105x3771. According to this website, the amount is 30-40 mg/kg.

Let us take very good quality phosphate, which is published value given by Benson, 2014.Trace Metals Levels in Inorganic Fertilizers Commercially Available in Nigeria: Article in Journal of Scientific Research and Reports. If we then compare what has been up taken and held in the grain vs supplied by the fertilizer as given in Table, you are correct, only a small quantity remains in the soil and a similar quantity enters the cereal grains. But the small quantity in the grains is the one causing many health issues.

[CDW: But that small quantity is NOT what is coming from the fertilizers. Onl

y a few parts in a trillion out of it is coming from fertilizers. The ambient Cd concentration may be like millions of times more than the concentration increment caused by the cadmium brought in by the fertilizer. Same argument for other heavy metal toxins]

It is very clear that the chelation of organometallics in nitrogen supply from urea can get transported directly to the grain.

Geological deposited Cd too get chelated, especially in the presence of large quantities of nitrogen in the soils. Please read Cadmium (II) Complexes of Amino Acids and Peptides (Newman et al., 2016) to give you a very good insight into the issues of heavy metals in foods.

[CDW: Newman ignores the role of Zn in soils. Zn which is in the same column as Cd in the periodic table usurps Cd in most reactions. Although there IS cadmium in sunflower seed and in shell fish, they are allowed to be sold in Europe because the amount of Zn far exceeds that of Cd by two to three orders of magnitude. Read my cadmium in fertilizers, soils paper. Or read Dr. Rufus Cheney, Advances in Agronomics, Volume 12]

Another aspect as pointed out before is bioaccumulation of heavy metals causing obesity, diabetics, and cancer. There are many papers on these subjects showing the cause and effect of HM. If we now compare Girandurukotte (GK) soils and Hambantota, GK soils are lethal. We can just look at the table of Valhos et al., 2021 and ignore the errors of syntax and typos, which was mentioned by Prof. Dhanapala.

[CDW: I have answered Valhos et al paper and I have submitted my manuscript to a journal. So I will not discuss these issues as yet. May be next month when I hear from the referees etc. Valhos et al ignores v well known medical and geological facts]

They have given the locations of the wells; thus, it is possible to repeat, which is not the case in most other reputed publications. If those agrochemicals are present in the wells, they should also be present as POPs in soils, thus further complexing the uptake of heavy metals present in the fertilizer. Biochar can remediate the soils and experimentation should be undertaken also to use other bio remedial measures to remove the POPs.

[CDW: Balassooriya et al also have given specific well data. The Valhos paper is a single time measurement, but does not say if it coincided with a pesticide application time. The value of the paper is that it shows that farmers are not careful enough to avoid pesticide contamination of their wells. But one has very good reasons to conclude that these pesticides are NOT the cause of CKDu., although they may cause other diseases including CKD]

The field trials of many experimentations indicated the replacement of 70% of urea and inorganic fertilizer with unstable biochar. You have already agreed on the principle of incorporating BFBFs/other biofertilizers to biochar for enhancing the yield and bringing about sustainable productions. Prof. Vitanage must give a counter argument to my explanation otherwise 1 kg of Urea is equal to 1 biochar (unstable) stands as a

rule of thumb because you have agreed that you are not able to evaluate biochemical transformation kinetics. You cannot withdraw what you ADMITTED. It is final.

[CDW: The relation between 1 kg of biochar and 1 kg of urea is not to be settled by some dubious biochemical kinetics, but by experiments. You know very well that ANY kinetic equation is a differential equation, and hence its solutions depend on the boundary conditions. In this case they are initial values of various nutrients, soil conditions pH, eH etc., as pointed out. Even if the kinetic equations are right, the answers for different boundary conditions will be different. Also, there are too many poorly known quantities and rate constants. Virtually nothing can be evaluated from the Hamiltonian of the system. So we need experiments, and not just theory.

Furthermore, the Michaels-Menton equation as used requires many assumptions for it to give a convenient closed-form solution. For example, the coupled equations form a set of rate equations from which we can obtain a closed-form solution that describes the evolution of concentration of the participants in an enzymatic reaction. To get this solution, assumptions must be made to reduce the complexity of the rate equations. One must make the *steady state approximation*, which assumes negligible rate of change in the concentration of the enzyme substrate complex in the course of the process considered. Furthermore, Michaels-Menten presupposes that *catalysis is irreversible* and that the *enzyme is not subject to product inhibition*. Many of these assumptions can be relaxed and then we can get solutions of varying types of kinetics on a computer. I haven't looked at it in detail, but probably the Ariyawansha et al extension can also be considered within this framework. But what is realistic has to be determined by experiments.

I only entered this debate because I highly respect Prof. Kulasooriya and Prof. Senevirathne as excellent scientists.

[CDW: We have not contested their competence as scientists. I began by contesting Chris Dharmakiri's contention that blue-green algae use in paddy fields and other microbial techniques were PROVEN technologies.

As for BFBF, the only supporting publication is the CABJ chapter which was shown to contain completely untenable unscientific data. The independent trial from Maha-Illuppllama also shows that BFBF claim of a full harvest with 50% chemical fertilizer is FALSE.

So, we have to go by what is in the public domain in regard to a product. You too have to go by what is published under controlled conditions, and not by what "the Botany Professor" said.]

They are helping farmers, agricultural officers, and extension services while bringing an income to NIFS from their promoted products. I believed that my scientific approach could resolve the issues to demonstrate the superiority of organic fertilizer as against inorganic. The latter causes many health issues and now require funds to rectify the pollution loads including the biomass still holding the applied heavy metals derived from the inorganic fertilizers in the fields. Therefore, HM laden compost should not be applied in the drive to replace inorganics. It will take many years to get rid of the organometallic chelated with hazardous chemicals persisting from the applications of glyphosate.

[CDW: glyphosate is a chelating agent. It has been shown to ameliorate soils containing cadmium, when earth worms once again begin to thrive, and the microbial biomass increases on application of glyphosate to the soil.

Urea wasted can be avoided, as it can be applied as solid urea-nanoparticles to the soil, and the nanoparticles can be designed for time release according to a sophisticated calendar. Unlike micro-organisms, inorganic materials can be precisely engineered to time release. Sri Lanka already has a nano-urea patent. Micro-organisms evolve and adapt, so a given microbial product will not necessarily work next year in a new habitat or even in the old habitat]

The economics of organic vs inorganic can be deduced from the prices of Urea. Urea prices are three times higher than last year. You can also find the prices of bamboo biochar in the websites. It is as good as coconut shell char because it has plate like structures.

Dr. N. Dharmawardena (your brother), the Chairman TRI is still waiting for largescale organic agriculture trials (we know the reasons for the delay), and he is supporting the biochar biofertilizer movement because he is an excellent biochemist and I admire his knowledge and the charismatic personality as much as you. Already several plantations use biochar biofertilizers. Now, most renowned compost manufacturers use unstable or stable char or both to increase CEC and augment nitrogen content in the compost. When you next come over to Sri Lanka, we will show you lushes tea plantations enriched with biofertilizers.

I have given many references and counter arguments, which you have ignored. It is not a debate between inorganic vs organic fertilizers, but a dispute between Chemists and bio-scientists.

[CDW- exactly so. The argument has to be settled by experiments. Not by statements expressing confidence and good faith in X, or Y and Z]

The geologists have already signalled their willingness to revisit their papers on CKDu. I am going to request the same from soil scientists. Let's hope you too will be enlightened.

Thanking you,

Kind regards,

BenBasnayake

Please refer to the attached tables

Fertilizer		Application	Total.
	mg/kg	Rate (kg/ha)	mg/ha
P2O5	2.59	60	155
Urea	2.67	225	601
	5.26	**285**	**1499**
Grain			
Edirisighe and Jinadasa, 2020			
<6.00- 261.786 µg/kg,		Harvest	Total
	mg/kg	kg/ha	mg/ha
Average	0.130893	5200	681
		7000	916
Remaing in soil @ 5200 kg/ha			**818**
Remaing in soil @ 7000 kg/ha			**583**

Table 2. Agrochemicals detected in domestic well in Wilgamuwa, Sri Lanka during 2018 water sampling from Shipley et al. (2022)[24].

Agrochemical	Number of detections	Concentration mean(median) (µg L^{-1})	Global drinking water guidelines (µg L^{-1})	Detections exceeding guidelines
Diazinon	139	2330 (1880)	7	139
p,p'-DDE	42	2440 (2260)	1	42
Propanil	41	20670 (2300)	175	41
Endosulfan II	39	2200 (2120)	62	39
o,p'-DDT	18	740 (540)	1	18
Inorganic		**(mgL^{-1})**	**(mgL^{-1})**	
Hardness	273‡	163 (130)	<60 (soft)	32
			<120 (moderate)	98
			<180 (hard)	64
			>180 (very hard)	79
Phosphate	273‡	0.45 (0.25)	0.05*	218