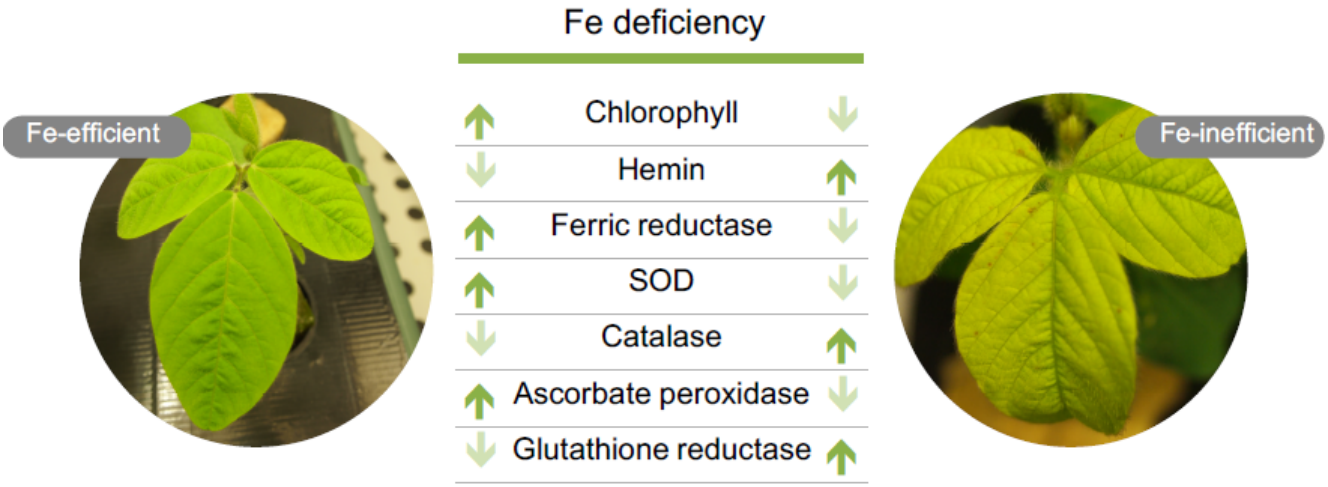
Are Iron chelates of humic/fulvic acids better or worse than synthetics?

Why Fe nutrition is problematic

Plants need substantial amounts of iron to thrive. However, iron is a finicky element, and will react with many substances to form solids that are unavailable for plant uptake. This is a specially common process under high pH, where iron can form insoluble carbonates, hydroxides, oxides, phosphates and even silicates. For this reason, plant scientists have – for the better part of the last 100 years – looked for ways to make Fe more available to plants, while preventing the need for strategies that aim to lower the pH of the soil, which can be very costly when large amounts of soil need to be amended.



The image above is taken from this paper on Fe deficiencies.

In hydroponics, the situation is not much better. While we can add as much Fe as we want to the hydroponic solution, the above processes still happen and the use of simple Fe salts (such as iron nitrate or iron sulfate) can lead to Fe deficiencies as the iron falls out of solution. This can happen quickly in root zones where plants aggressively

increase the pH of solutions through heavy nitrate uptake.

For a better understanding of the basics of soil interactions with microbes, plants and the overall Fe cycle, I suggest reading this review (6).

Synthetic chelates to the rescue

The above problems were alleviated by the introduction of synthetic iron chelates in the mid 20th century. The chelating agents are organic moieties that can wrap around the naked metal ions, binding to their coordination sites. This kills their reactivity and ensures that they do not react with any of the substances that would cause them to become unavailable to plants. Plants can directly uptake the chelates, take the iron and push the chelate back into solution, or they can destroy the chelate and use its carbon within their metabolism.

Chelates can bind Fe very strongly though, and this is not desirable for some plants that do not have the enzymatic machinery required to open these “molecular cages”. Studies with monocots (1) – which are grasses – have often found that these plants respond poorly to Fe supplementation with molecules like Fe(EDDHA), a very powerful chelate. So powerful in fact, that not even the plants can get the Fe out. For these plants, weaker chelates often offer better results, even at higher pH values.

Another problem is that many of the synthetic chelates are not very good at high pH values. When the pH reaches values higher than 7.5, chelates like EDTA and DTPA can have problems competing with the much more strongly insoluble salts that form at these pH values. The chelated forms are always in equilibrium with the non-chelated forms and the minuscule amount of the non-chelated form drops so quickly out of solution that the entire chelate population can be depleted quite quickly. (2)

Chelates that respond well to high pH values, like EDDHA, are often much more expensive. In the case of EDDHA, the presence of a lot of isomers of the EDDHA molecule that are weaker chelates, also creates problems with quality control and with the overall strength of each particular EDDHA source. The EDDHA is only as good as its purification process, which makes good sources even more expensive (3, 4).

An additional concern is the oxidation state of the Fe. While Fe chelates are usually prepared using ferrous iron (Fe^{2+}), these iron chelates are quickly oxidized in solution to their ferric iron (Fe^{3+}) counterparts, especially when the solution is aerated to maintain high levels of oxygen. Since Fe^{3+} is both more tightly bound to chelates and more reactive when free – so more toxic when taken up without reduction – plants can have an even harder time mining Fe^{3+} out of chelates (5, 7).

Then there are naturally occurring chelates

There are many organic molecules that can form bonds with the coordination sites of Fe ions. Some of the reviews cited before go into some depth on the different groups of organic molecules that are excreted by both plants and microorganisms as a repose to Fe deficiency that can lead to improved Fe transport into plants. Some of these compounds are also reductive in nature, such that they can not only transport the Fe, but reduce it to its ferrous form such that it can be handled more easily by plants.

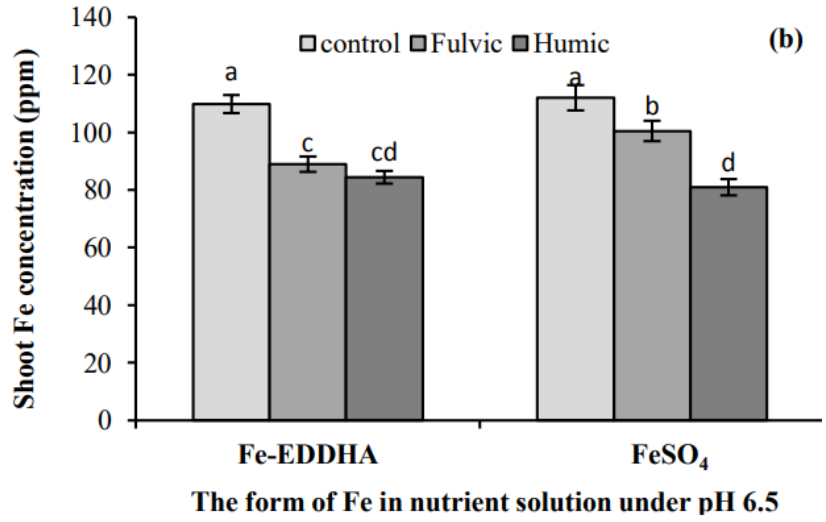
Among the organic compounds that can be used for Fe chelation, humic and fulvic acids have attracted attention, as they can be obtained at significantly low costs and are approved for organic usage under several regulations. You can read more

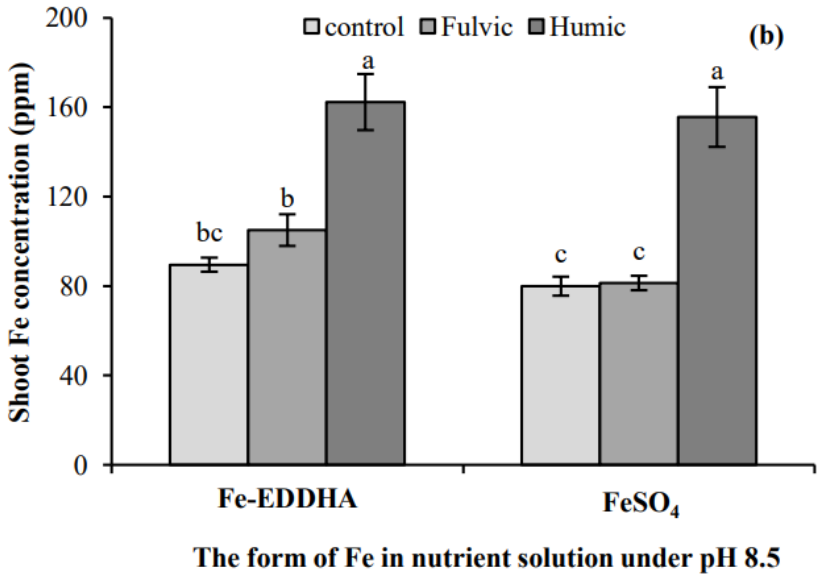
about these substances in some of my previous posts about them (8, 9). In particular, humic acids are more abundant and are formed by larger and more complex molecules compared to fulvic acids.

The ability of these substances to chelate Fe is much weaker than that of synthetic chelates. The pKb shows us the strength of the binding equilibrium of the chelate with the free metal ion (you can see the values for many metals and chelating agents here). The value for EDTA is 21.5 while that of most humic and fulvic acids is in the 4-6 range (10). This is a logarithmic scale, so the difference in binding strength is enormous. *To put things into perspective, this difference in binding strength is of the same magnitude as the difference between the mass of a grain of sand and a cruise ship.*

Comparing synthetic and fulvic/humic acid chelates

There aren't many studies comparing synthetic and humic/fulvic acid chelates. One of the most explicit ones (11) compares solutions of Fe sulfate (which we can consider unchelated) and Fe(EDDHA) after additions of fulvic or humic acids in the growth of Pistachio plants. At pH values close to those generally used in hydroponics (6.5) there is hardly any difference between any of the treatments while at higher pH values we have substantially better uptake of Fe in both the EDDHA and unchelated iron treatments when supplemented with either fulvic acid or humic acid.





Images at pH 8.5 of Fe in shoots from the Pistachio study (11)

The idea of using humic acids as a compliment of traditional chelate based fertilization to alleviate high fertilization costs has also been studied in citrus (13). This study confirms some of the findings of the previous one, where additions of humic acids to solutions already containing Fe(EDDHA) provided a more beneficial role than simply the use of the pure humic acid substances or pure Fe(EDDHA) fertilization. Another study on citrus (14) showed that humic acid applications could in fact provide Fe supplementation in calcareous soils (these are soils with high pH values). This shows how humic acid fertilization can rival Fe-EDDHA fertilization.

In another study of leonardite iron humate sources and EDDHA in soybean roots (12) it is apparent that accumulation of Fe

in shoots and roots is much worse under the humic acid treatments. In the conclusions of the paper, it is highlighted that the high molecular mass of the leonardite constituents might block the roots of the soybean plants, therefore making it difficult for the plant to transport Fe. However, this study does show that the accumulation of these humic acids in the root zone does promote a decrease in the expression of genes that create Fe transporters and Fe reducing enzymes, pointing that the plant is indeed under less Fe deficiency stress. Another important point is that cycling the humic acid application promotes the absorption of accumulated humic acids, cleaning the roots and allowing for better transport of the Fe in the roots.

In a separate study with humic acid + $FeSO_4$ applications compared to Fe(EDDHA) in sweet cherry (13) it was found that the humic acid, when supplemented with unchelated iron, increased Fe tissue as much as the Fe(EDDHA) applications. This was consistent across two separate years, with the second year showing a statistically significant increase of the humic acid treatment over the Fe(EDDHA).

How does this work

An interesting point – as I mentioned before – is that humic/fulvic acids are *incredibly weak* chelating agents. This means that they should release their Fe to the bulk of the solution, which should lead to Fe depletion and deficiencies, as the Fe precipitating mechanisms are thermodynamically much more stable. However this is not what we consistently observe in the studies of Fe nutrition that try to use humic/fulvic acids, either with or without the presence of additional synthetic chelates.

The reason seems to be related with the kinetics of Fe release from these substances. While the stability constants of the chelates are weak – therefore they will release and

precipitate in the long term – the bulkiness of the ligands and the complex structures surrounding the metals, makes it hard for the metal to actually escape from the chelate structures around it. However, the fact that the bonding is thermodynamically weak, ensures that the metal can be easily transported once it leaves the organic chelate structure.

Another point is that humic/fulvic substances are reductive in nature, which means that they will protect Fe^{2+} from oxidation by either microbes or oxygen dissolved in solution. They are also sometimes able to reduce Fe^{3+} present in solution back to Fe^{2+}, which can help with the uptake of this Fe by the plant's root system.

The nature of the above structures and their reductive power depends fundamentally on the actual humic/fulvic acid used, so – as with all cases pertaining to fulvic/humic substances – the source you use will play a big role in determining the final outcome you get.

What chelates are the best?

Current research shows that Fe(EDDHA) and similar chelates, despite their high stability constants, are not perfect. While they can provide ample iron for dicots and can cure Fe deficiencies in the large majority of cases for these plants, these strong chelates are often very expensive and their use as sole Fe sources might be impractical for many cases in traditional agriculture and hydroponics/soilless growing.

The use of humic/fulvic acids complimented with either unchelated Fe or with some lower proportion of stronger iron chelates, seems to be a better overall choice in terms of both plant uptake and economic expense. As shown by several studies mentioned in this post, the effect of humic/fulvic acids and synthetic chelates might actually be synergistic, with both providing different advantages that can be complimentary in

hydroponic solutions. These humic/fulvic acid solutions might also be much more favorable for monocot species, where the use of highly stable Fe(EDDHA) chelating agents does not cure deficiency symptoms.

The take away here is that chemical chelate strength is not the only thing to consider. The kinetics of the chelate dissociations, as well as how the chelates interact with the root system, for example how the plant can actually take the Fe outside of the chelating system, are all very important to establish whether the Fe is effectively absorbed and transported by the plants.

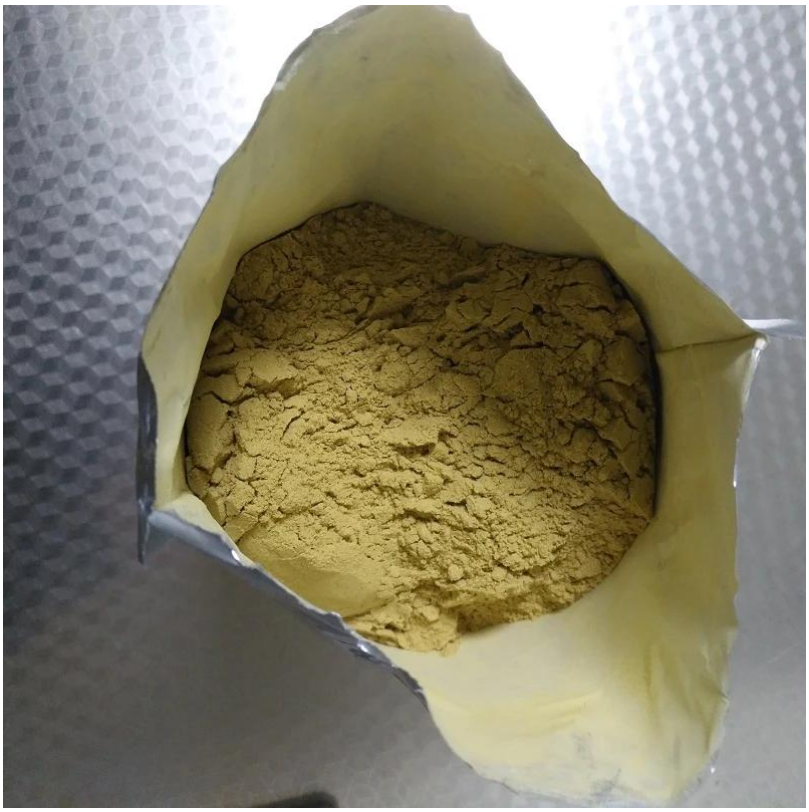
Please note that the topic of Fe nutrition is extremely extensive and while the above is intended to be a short introduction to the topic of humic/fulvic acids and how they compare to synthetic chelates, it is by no means an exhaustive literature review.

Are you using fulvic or humic acids for Fe nutrition? Let us know what your experience is in the comments below.

A great trick to higher chelate stability in hydroponics

The stability of micronutrients in hydroponic solution has been studied in depth during the last 5 decades (1). The EDTA molecule was the first cheap synthetic ligand that created highly stable chelates that could be used to stabilize heavy metals in solution. After this, efforts to create more stable chelates continued, with the introduction of HEDTA, DTPA,

EDDHA, and other synthetic ligands. However, the stability of iron in solution still remains a problem. This is due to the chemistry of heavy metals in solution and the issues that arise as root zone chemical conditions change in a hydroponic crop. In this post we will discuss a simple trick, to increase the stability of the cheaply available iron EDTA chelate, the most commonly used in nutrient solutions. **Note, the term "heavy metal" in this post is used to refer to the transition metals used in hydroponics, mainly Fe, Zn, Mn and Cu.**



$Na_2FeEDTA$, one of the most commonly used Fe chelates in hydroponics.

Chelate stability

The stability of chelates is dominated by three competing forces. The first is the acid/base equilibrium of the ligand. Ligands like EDTA are only able to chelate Fe when their active sites are not occupied by hydrogen ions. As the pH goes down, these sites become occupied and the $EDTA^{-4}$ turns into

$HEDTA^{-3}$, then H_2EDTA^{-2}, H_3EDTA^{-1}, and finally H_4EDTA. This process frees the heavy metal ions as the concentration of the active ligand ($EDTA^{-4}$) drops to near zero values. At very acidic pH values, the Fe^{2+} will effectively become fully unchelated due to this effect, although this does not happen to a very large extent at the pH values we see in hydroponics.

The second effect has to do with the affinity of the ligand for the heavy metal. This is what we call the "stability" of the chelate. It is measured through the use of the equilibrium constant of the reaction of the metal with the ligand. The larger this value, the bigger the stability of the chelate will be and the less free metal we will have in solution. For more information about this, you can read this previous post, where I share a table with a lot of stability constants for different ligands and heavy metals.

The third is the precipitation of free heavy metal ions by the formation of insoluble solids. This can be quite critical, as several of the solids that can form in hydroponics, mainly hydroxides, and phosphates, have very low solubility values. These can be compared by using the equilibrium constant of the solid with the ions in solution, what we call the Ksp in chemistry. The smaller the Ksp, the more insoluble a substance is. When these solids precipitate they take ions away from the solution and these are regenerated by the chelated heavy metal equilibrium reaction. This depletes the heavy metal slowly from the solution.

Free heavy metal ions

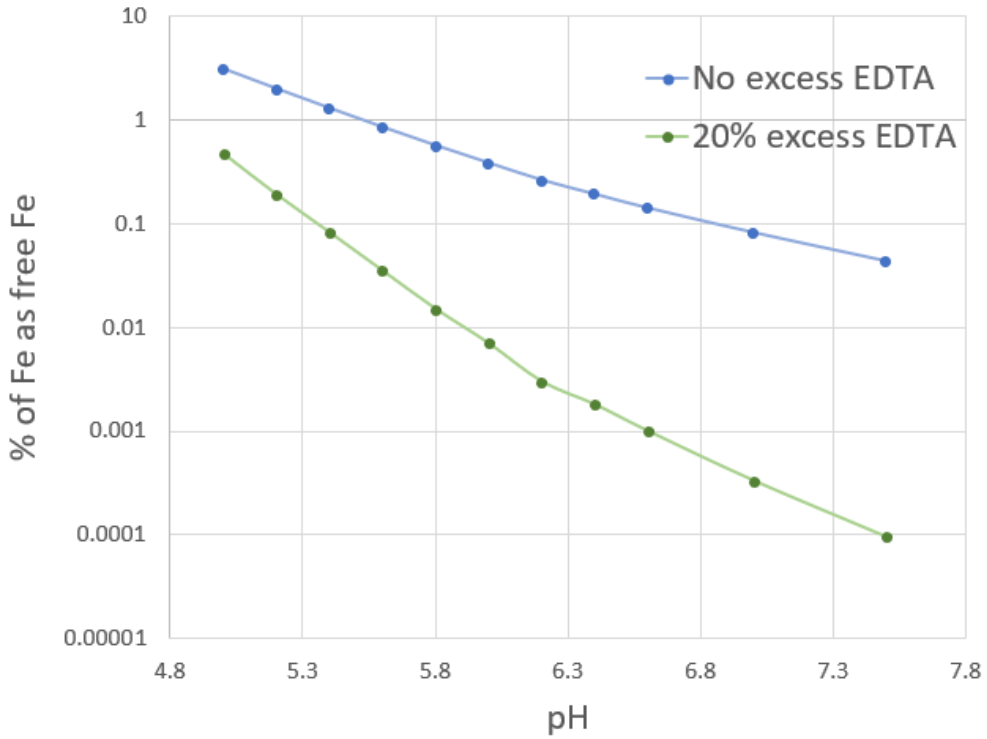
Since free heavy metal ions are the ones that can precipitate and become unavailable, what we desire is to lower the amount of free heavy metal ions in solution and increase the percent of chelated ions. Whenever you put a chelated heavy metal source in solution, like $Na_2FeEDTA$, the chelate goes into

equilibrium with its unchelated form and all the acid/base species of the ligand's equilibrium reactions. This means that a percentage of the Fe becomes effectively unchelated. **In a solution where 1ppm of Fe from Na_2FeEDTA is added, P is added at 30ppm and the pH is set to 6, around 0.38% of the Fe will be unchelated**.

As the pH increases the amount of free Fe actually decreases – as the acid/base equilibrium of the ligand shifts towards the base forms – but the concentration of other ions that can precipitate really insoluble salts, like phosphate or hydroxide, increases dramatically. At pH values above 7, even a small fraction of free Fe can lead to precipitation of some Fe salts. This is why iron EDTA chelates are not considered to be stable in basic pH, not because the chelate itself is unstable, but because there are even more stable Fe solids that can form and precipitate out the Fe.

A simple trick to alleviate the issue

Traditionally, the issue of having unchelated heavy metals has been approached by creating stronger chelates. DTPA, which has much higher stability constants, is able to generate much lower amounts of Fe, which leads to lower precipitation. The equilibrium constant with some isomers of EDDHA is actually so high, that no Fe solids are formed across almost the entire pH window in water. However, these chelates are more expensive, and – in the case of EDDHA – the presence of several different isomers complicates the situation.



Solution always has 1ppm of Fe added as $Na_2FeEDTA$ with 30ppm of P. The above was calculated using a system of equations accounting for all the EDTA and phosphate acid/base equilibria, as well as the heavy metal chelation.

A very simple trick to partially solve the problem is to add an excess of chelating agent into the hydroponic solution. If you're using EDTA, adding Na_2H_2EDTA on top of the heavy metal chelates can greatly help reduce the amount of free heavy metal in solution. This EDTA will also not remain unbound, as it will quickly chelate Mg and Ca in solution. These Ca and Mg chelates, will act as a reserve of ligand to ensure that almost all heavy metal ions are chelated. A 20% molar excess can generate dramatic results in the case of Fe^{2+}, as shown in the image above. This 20% "reserve" ligand, reduces the amount of free Fe by a factor of 10-100x, depending on the pH. Note that although the above slows down any precipitation reactions – as little free Fe is available – the hydroxide and phosphate ions will still win if the pH increases enough, as the stability constant of the Fe EDTA reaction remains the same.

To give a 20% excess of EDTA in molar terms, add 1.2mg/L of disodium EDTA to the final nutrient solution for every 1ppm of

Fe. You can also add a 100% molar excess with no ill effects on plants, which will provide a more pronounced effect.

Conclusion

Adding a chelated heavy metal form to a hydroponic solution does not ensure that the metal will always be chelated. The chemical equilibria that exist with the free form of the heavy metal always happen and will always generate some percentage of free, unchelated metal. By adding an excess of the chelating agent, in this case, Na_2H_2EDTA, we can strongly displace the equilibrium and reduce the amount of free heavy metal present. The lower amount of heavy metal increases the pH stability window of the chelate and reduces the precipitation issues that happen as a consequence of free heavy metal ions being present in solution.

Do you add excess chelating agent to your nutrient solutions? Let us know about your experience in the comments!

The stability of metal chelates

When you get introduced to hydroponics and nutrient solution chemistry, one of the first concepts that you learn is chelation. A chelate is a molecule formed by a metallic ion and a chelating agent – which is also referred to as a ligand – where the metal ion is wrapped around very tightly by this ligand. The job of the chelating agent is to keep the heavy metal ion shielded from the environment, allowing it to exist in solution without forming potentially insoluble compounds that will take it out of the nutrient solution. However, these

chelates can be unstable or too stable, both of which can hinder the availability of the nutrient to plants. In this post, we're going to talk about what determines the stability of a metal chelate and how you can know if a given chelate will be able to fulfill its job in a hydroponic environment.



$$Kb = \frac{|ML|}{(|M| \times |L|)}$$

A simplified view of the chemical equilibrium formed |M| refers to the concentration of the free metallic ion, |L| the ligand concentration and |ML| the chelate concentration. Charges are omitted for simplicity.

Since chelates are formed by the reaction of a metallic ion – most commonly a cation – which a ligand, a chemical equilibrium is established between the free metallic ion, the ligand, and the chelate. Every second, there are lots of chelate molecules being formed from reactions between metallic ions and ligands, and free metallic ions and ligands are being formed from the disassembly of the chelate. The process is in equilibrium when the rates of assembly and disassembly are the same. The equilibrium constant – also known as the stability constant or Kb – tells us how displaced this equilibrium is towards the product (in this case the chelate). When the Kb value is large, the concentration of the chelate at equilibrium is very large, while when Kb is small, the opposite is true. Since these numbers are usually very large for chelates, we express them as pKb which is -Log(Kb). These constants depend on temperature, but their values are independent of other chemical reactions. However, things like pH can affect the concentration of ligand or metal cation, which can affect the concentration of chelate, since the

equilibrium constant’s value remains the same.

	Al(III)	Ba	Ca	Co(II)	Cu	Fe(II)	Fe(III)	Hg	Mg	Mn	Ni	Sr	Zn
Acetic acid		0.39	0.53	2.24				3.7d	0.51		0.74	0.43	1.03
Adenine													
Adipic acid		1.92	2.19		3.35								
ADP		2.36	2.82	3.68	5.9				3.11	3.54	4.5	2.5	4.28
Alanine		0.8	1.24	4.82	8.18					3.24	5.96	0.73	5.16
b-Alanine					7.13						4.63		4
Albumin			2.2										
Arginine						3.2				2			
Ascorbic acid			0.19									0.35	
Asparagine			0									0.43	
Aspartic acid		1.14	1.16	5.9	8.57				2.43	3.74	7.12	1.48	2.9
ATP		3.29	3.6	4.62	6.13				4	3.98	5.02	3.03	4.25
Benzoic acid					1.6						0.9		0.9
n-Butyric acid		0.31	0.51		2.14				0.53			0.36	1
Casein			2.23										
Citraconic acid			1.3									1.3	
Citric acid		2.3	3.5	4.4	6.1	3.2	11.85	10.9d	2.8	3.2	4.8	2.8	4.5
Cysteine				9.3	19.2	6.2		14.4d	< 4	4.1	10.4		9.8
Dehydracetic acid					5.6						4.1		
Desferri-ferrichrysin							29.9						
Desferri-ferrichrome							29						
Desferri-ferrioxamin E				11.8	13.7		32.5				12.2		12
3,4-Dihydroxybenzoic acid			3.71	7.96	12.8				5.67	7.22	8.27		8.91
Dimethylglyoxime					11.9						14.6		7.7
O,O-Dimethylpurpurogallin			4.5	6.6	9.2				4.9		6.7		6.8
EDTA	16.13	7.78	10.7	16.21	18.8	14.3	25.7	21.5d	8.69	13.6	18.6	8.63	16.5
Formic acid		0.6	0.8		1.98		3.1					0.66	0.6
Fumaric acid		1.59	2		2.51					0.99		0.54	
Globulin			2.32										
Gluconic acid		0.95	1.21		18.3				0.7			1	1.7
Glutamic acid		1.28	1.43	5.06	7.85	4.6			1.9	3.3	5.9	1.37	5.45
Glutaric acid		2.04	1.06		2.4				1.08			0.6	1.6
Glyceric acid		0.80b	1.18						0.86			0.89	1.8
Glycine		0.77	1.43	5.23	8.22	4.3	10	10.3	3.45	3.2	6.1	0.91	5.16
Glycolic acid		0.66	1.11	1.6	2.81		4.7		0.92			0.8	1.92
Glycylglycine			1.24	3	6.7	2.62	9.1		1.34	2.19	4.18		3.91
Glycylsarcosine				3.91	6.5					2.29	4.44		
Guanosine				3.2	6	4.3			3		3.8		4.6
Histamine				5.16	9.55	9.6	3.72				6.88		5.96
Histidine				7.3	10.6	5.89	4			3.58	8.69		6.63
b-Hydroxybutyric		0.43	0.6						0.6			0.47	1.06
3-Hydroxyflavone				9.91	13.2								9.7
Inosine				2.6	5	3					3.3		
Inosine triphosphate			3.76	4.74					4.04	4.57			

Iron-free ferrichrome							24.6						
Isovaleric acid			0.2		2.08								
Itaconic acid			1.2		2.8						1.8	0.96	1.9
Kojic acid	7.7		2.5	7.11	6.6		9.2		3		7.4		4.9
Lactic acid		0.55	1.07	1.89	3.02		6.4		0.93	1.19	2.21	0.7	1.86
Leucine				4.49	7	3.42	9.9			2.15	5.58		4.92
Lysine							4.5			2.18			
Maleic acid		2.26	2.43		3.9					1.68	2	1.1	2
Malic acid		1.3	1.8		3.4				1.55	2.24		1.45	2.8
Methionine						3.24	9.1				5.77		4.38
Methylsalicylate					5.9		9.77						
NTA	>10	4.82	6.41	10.6	12.7	8.84	15.87		5.41	7.44	11.3	4.98	10.45
Orotic acid				6.39c							6.82		6.42
Ornithine				4.02	6.9	3.09	8.7			<2	4.85		4.1
Oxalic acid	7.26	2.31	3	4.7	6.3	>4.7	9.4		2.55	3.9	5.16	2.54	4.9
b-Phenylalanine					7.74	3.26	8.9						
Pimelic acid										1.08			
Pivalic acid			0.55		2.19								
Polyphosphate			3		3.5	3			3.2	5.5	3		2.5
Proline						4.07	10			3.34			
Propionic acid		0.34	0.5		2.2		3.45		0.54			0.43	1.01
Purine					6.9						4.88		
Pyrophosphate			5		6.7		22.2		5.7		5.8		8.7
Pyruvic acid			0.8		2.2								
Riboflavin				3.9	<6					3.4	4.1		<4
Salicylaldehyde				4.67	7.4	4.22	8.7		3.69	3.73	5.22		4.5
Salicylic acid	14.11			6.72	10.6	6.55	16.35		4.7	2.7	6.95		6.85
Sarcosine				4.34	7.83	3.52	9.7				5.41		
Serine			1.43			3.43	9.2				5.44		
Succinic acid		1.57	1.2	2.08	3.3		7.49		1.2	2.11	2.36	0.9	1.78
(+)-Tartaric acid		1.95	1.8		3.2		7.49		1.36		3.78	1.94	2.68
Tetrametaphosphate		4.9	5.2		3.18				5.17		4.95	2.8	
Threonine						3.3	8.6						
Trimetaphosphate			2.5		1.55				1.11	3.57	3.22	1.95	
Triphosphate		6.3	6.5		9.8				5.8			3.8	9.7
Tryptophan							9						
Uridine diphosphate									3.17				
Uridine triphosphate			3.71	4.55					4.02	4.78			
n-Valeric acid		0.2	0.3		2.12								
Valine					7.92	3.39	9.6			2.84	5.37		5
Xanthosine				2.8	3.4	<2					3		2.4

This table was originally present in a website that no longer exists. The data is taken from the NIST reference of heavy metal complexes.

The table above shows you the pKb values for different metal ions and different ligands or chelating agents. Since the pKb scale is logarithmic, a difference of 1 indicates an order of

magnitude higher stability. You can also find additional references to other stability constants in this link. These constants allow us to predict which chelates will be formed if different metallic cations and ligands are present. Let's say we have a solution that contains Ca2+ and Fe3+ and we add a small amount of sodium citrate, what will happen? Since the constant for Ca2+ is 3.5 but that of Fe3+ is 11.85, citrate will chelate around 1 billion Fe3+ ions for every Ca2+ ion it chelates. In practice, this means that all the Fe3+ that can be chelated will be, while Ca2+ will remain as a free metallic ion. However, if we have Fe^{2+} instead of Fe^{3+} then Fe^{2+} has a constant of only 3.2, which means that one molecule of Fe^{2+} will be chelated for every 3 of Ca^{2+}, meaning we will have around 25% of all the chelate formed as a chelate formed by Fe^{2+} and 75% as a chelate formed by Ca^{2+}.

We can see in this manner how chelating only one heavy metal can lead to problems. Imagine that you purchase Iron EDTA and add it to your nutrient solution, but you have added Manganese from Manganese sulfate. Upon addition, the FeEDTA chelate will disassemble to generate as much Fe^{2+} and free EDTA as dictated by the equilibrium constant and the free EDTA will then get into equilibria with all the other heavy metals, since the constant with Mn is 13.6 and that of Fe is 14.3 the ligand will redistribute itself so that it complies with all the chemical equilibria present. This means that for every 7 Fe^{2+} cations that are chelated we will have around 1 Mn^{2+} containing chelate, so you will lose around 14% of the chelated Fe in order to chelate free Manganese. That free Fe^{2+} will be unstable and precipitate out, which will shift the equilibrium and cause us to lose more of the Fe chelate. This is how competing equilibria can lead to the slow but sure depletion of available cations in solution.

With the above references and charts, you should now be able

to look into any chelating agent you want to use and determine how good of a choice it is for your solution and what is likely to happen once you put that chelate in. The ligand will chelate different metals in order to comply with all the equilibrium constants, so it is up to you to add enough so that all heavy metals are satisfied or add ligands whose affinity for a given ion is so high that the others are just unable to compete for it, almost regardless of their concentration.