Florida Department of Environmental Protection

Bob Martinez Center
2600 Blair Stone Road
Tallahassee, Florida 32399-2400

Rick Scott
Governor

Carlos Lopez-Cantera
Lt. Governor

Noah Valenstein
Secretary

September 1, 2017

Via Electronic Mail to Roger Kubala at: rakubala@terrahydrochem.com

Mr. Roger Kubala, President
TerraHydroChem, Inc.
217 Deborah Drive
New Braunfels, Texas 78130

Re: **TerraHydroChem™ Products:**
TerraSolve-100 (TS-100), **TerraCleanse-1200** (TC-1200), **TerraCleanse-1200nzvi** (TC-1200nzvi), **TerrOx, TerraCleanse-nZVI** (TC-nZVI)

Dear Mr. Kubala:

The Florida Department of Environmental Protection's Division of Waste Management (Division) hereby accepts TerraHydroChem™ products for remediation petroleum, chlorinated hydrocarbons, and other suitable contaminants in groundwater and soil.

TerraHydroChem™ products, formerly known as Bio Blend Technologies products (and also known as Star System), were originally accepted by the Division on July 5, 2011. The formulations have not changed since that time, but the names of the formulations, the name and address of the firm, and the numbering of some of the applicable Florida Administrative Code rules have changed. The name of the firm is now TerraHydroChem, Inc. The names of the reagents are now as follows:

- Bio Blend-106 (a mix of anionic and nonionic surfactants) is now TerraSolve-100 (TS-100),
- Bio Blend-108 (a mix of anionic and nonionic surfactants) is now TerraCleanse-1200 (TC-1200),
- Bio-Blend-800 (a mix of nonionic surfactant and bioremediation nutrients) is now TerraCleanse-1200nzvi (TC-1200nzvi),
- Sodium Percarbonate (an oxidizer) is now TerrOx,
- and Zero-Valent Iron (a reducing agent) is now TerraCleanse-nZVI (TC-nZVI).

The subject updated acceptance letter also addresses changed contact information for TerraHydroChem™ products manufacturer/ distributer and the numbering of some of the applicable Florida Administrative Code rules as well.

The five reagents listed above are not used simultaneously, but the three TerraHydroChem™ formulations [TerraSolve-100, TerraCleanse-1200, and TerraCleanse-1200nzvi] are typically used sequentially during different phases of the remediation. The selection of which reagent should be used will depend on the type of contaminants being cleaned up and whether the cleanup strategy is soil-washing/biostimulation, oxidation, or reduction. Enclosure 1 contains Voucher for Disclosure for the proprietary ingredients for TerraSolve-100, TerraCleanse-1200, and TerraCleanse-1200nzvi. Enclosure 2 contains regulatory information. Enclosure 3

contains supplemental information. Enclosure 4 provides calculation of alternative groundwater cleanup Target Level (AGCTL) for ammonia.

For vadose remediation, where the underlying groundwater will not be affected by the leaching of TerraHydroChem™ formulations, there are no special concerns beyond those that would normally need to be addressed in preparing a Remedial Action Plan and conducting a cleanup in accordance with Chapters 62-780 and 62-777, F.A.C. However, for in situ groundwater remediation, via direct injection of TerraHydroChem™ formulations into an aquifer, there are underground injection control regulations that must be observed. Since injection-type, in situ aquifer remediation is likely to be the most common application of TerraHydroChem™ formulations, the bulk of the regulatory requirements discussed herein will be directed to that topic.

While the Florida Department of Environmental Protection (FDEP) does not provide endorsement of specific or brand name remediation products or processes, it does recognize the need to determine their acceptability from an environmental standpoint with respect to applicable rules and regulations, and the interests of public health safety. Vendors, upon receipt of an acceptance, must market their product or process on its merits regarding performance, cost, and safety in comparison to competing alternatives in the marketplace. This acceptance letter shall not be construed as either an approval of the product or a certification of its performance.

It is not a requirement that a remediation product or process obtain an acceptance from the Department in order to be proposed for use in a site-specific Remedial Action Plan, but the plan must contain information to show that it meets all applicable and appropriate rules and regulations. For TerraHydroChem™ products listed in this letter, a copy of this acceptance letter containing regulatory compliance advice should be included in the appendix of each site-specific Remedial Action Plan that proposes its use.

The Department reserves the right to revoke its acceptance of a product or process if it has been falsely represented. Additionally, Department acceptance of any product or process does not imply it has been deemed applicable for all cleanup situations, or that it is preferred over other treatment or cleanup techniques in any particular case. A site-specific evaluation of applicability and cost-effectiveness must be considered for any product or process, whether conventional or innovative, and adequate site-specific design details must be provided in a Remedial Action Plan. If you have any questions, contact Elena Compton at (850) 245-8911, through Mail Station 4580 at the letterhead address, or by e-mail at Elena.Compton@dep.state.fl.us.

Sincerely,

Elena C. Compton

Elena Compton, M.S., P.E.
Professional Engineer II
PRP Team 2, FDEP
850-245-8911

Enclosures: (1) Voucher; (2) Regulatory Information; (3) Supplemental Information; (4) Calculation of AGCTL for Ammonia

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Mr. Roger Kubala, President
TerraHydroChem, Inc.
217 Deborah Drive
New Braunfels, Texas 78130

Re: **Proprietary Ingredients Voucher**
for TerraHydroChem™ Products: TS-100, TC-1200, TC-1200nzvi

Dear Mr. Kubala:

The July 5, 2011, Division of Waste Management's acceptance letter acknowledged receipt of confidential disclosures dated May 18, 2011, from TerraHydroChem, Incorporated. The disclosures provided the proprietary proportions of ingredients in TerraHydroChem™ Products (TS-100, TC-1200, TC-1200nzvi).

In the July 5, 2011, acceptance letter, the Division vouched for the subject formulations content and provided advice in Enclosure 2 on how to comply with applicable regulations of the Florida Administrative Code (F.A.C.) when each of these three TerraHydroChem™ products is used for the cleanup of contamination in accordance with a Department-approved, site-specific Remedial Action Plan. The Department, in offering its advice, has been careful to mention only enough general information about the chemical species and parameters that must be monitored by users in order to comply with Underground Injection Control regulations, but not so much information as to compromise the proprietary aspects of the products.

For Underground Injection Control purposes, injection-type aquifer remediation plans must specify both the volume and the complete chemical composition of the fluid to be injected. But since the details of the ingredients and their proportions in TS-100, TC-1200, TC-1200nzvi are proprietary, it will suffice to indicate just the fluid volume and concentration of each product to be injected, and then provide a note that a confidential disclosure of the proprietary details has already been submitted to the Department and accepted. Reference should be made to this voucher, and a copy of it should be included as an appendix to the plan. If you have any questions, contact Elena Compton at (850) 245-8911, through Mail Station 4580 at the letterhead address, or by e-mail at Elena.Compton@dep.state.fl.us.

Sincerely,

Elena C. Compton

Elena Compton, M.S., P.E.
Professional Engineer II
PRP Team 2, FDEP
850-245-8911

1. Groundwater cleanup standards: The onus shall be on users of TerraHydroChem, Inc., to ensure that all applicable groundwater standards will be met at the time of project completion for the contaminants of concern being remediated, and any by-products produced as a result of chemical or biochemical reactions induced or assisted by TerraHydroChem™ Products (TS-100, TC-1200, TC-1200nzvi, TerrOx, TC-nZVI). The following chapters of the Florida Administrative Code (F.A.C.) are cited: Chapter 62-550, F.A.C., for primary and secondary water quality standards; Chapter 62-520, F.A.C., for groundwater classes and standards; Chapter 62-522, F.A.C., for groundwater permitting and monitoring requirements; Chapter 62-528, F.A.C., for underground injection control, particularly Part V, for Class V, Group 4 aquifer remediation projects; Chapters 62-780, 62-782, and 62-785 F.A.C., for cleanup criteria; and Chapter 62-777, F.A.C., for cleanup target levels; and Chapter 62-780, F.A.C., for allowance of alternative cleanup target levels and conditional closure requirements.

2. Injection well permit: Per Rule 62-528.630(2)(c), F.A.C., the issuance of an enforceable, site-specific Remedial Action Plan Approval Order by the Department for injection-type aquifer remediation constitutes the granting of a Class V injection well construction/clearance permit.

3. Underground Injection Control (UIC): Remedial Action Plans proposing injection-type aquifer remediation shall include the information required by Rules 62-528.630(2)(c)1 through 6, F.A.C., for the purposes of the UIC program. Reviewers of those plans, upon issuance of a Department-enforceable Remedial Action Plan Approval Order, must transmit this information to the UIC program in Tallahassee by submitting a completed copy of the "UIC Notification". The notification is in the form of a memorandum currently located on the Internet at www.dep.state.fl.us/waste/categories/pcp/pages/innovative.htm.

4. General information about temporary Zones of Discharge (ZOD): For groundwater remediation, the composition of a fluid to be injected must meet the primary and secondary drinking water standards set forth in Chapter 62-550, F.A.C., and the minimum groundwater criteria of Chapter 62-520, F.A.C. [and Chapter 62-777], pursuant to UIC Rule 62-528.600(2)(d), F.A.C. Aquifer remediation products that do not meet these requirements must seek relief from water quality criteria by one of two mechanisms as follows. Permission for a temporary ZOD may be obtained via Rule 62-520.310(8)(c), F.A.C. If permission for a ZOD cannot be obtained by rule, then it will be necessary to seek a variance from Department rules in accordance with Section 120.542, Florida Statutes.

   Rule 62-520.310(8)(c), F.A.C., allows for a temporary ZOD for closed-loop re-injection systems, for the prime constituents of the reagents used to remediate site contaminants, and for groundwater secondary standards. In order to obtain permission for a temporary ZOD by rule, a site-specific Remedial Action Plan must indicate: (a) the chemical ingredients of concern in the fluid to be injected that will be present in excess of groundwater standards; (b) the size of the ZOD that is needed; (c) the amount of time that the ZOD will be needed; and (d) a plan for monitoring the injected chemical ingredients of concern.

   The size of the temporary ZOD will usually be the injection well radius of influence when the treatment system is a single injection point. For a multiple point system, the ZOD can usually be expressed and illustrated as the total area covered by all the injection points, located side-by-side with overlapping radii of influence.

5. Site-specific Remedial Action Plans shall describe:

   a) The volume and concentration of the following proprietary aqueous TerraHydroChem™ formulations: TerraSolve-100 (TS-100), TerraCleanse-1200 (TC-1200), and TerraCleanse-1200nzvi (TC-1200nzvi) slurry/solution that will be injected.

   b) The volume, concentration, and the complete chemical composition of the following aqueous TerraHydroChem™ formulations: TC-nZVI (Sodium Bicarbonate) and TerrOx (Zero-Valent Iron).

6. Specific ZOD information for TerraHydroChem™ products: TS-100, TC-1200, TC-1200nzvi, TerrOx, TC-nZVI:

   a) **TerraSolve-100** (TS-100): The typical injection (or re-injection) volumetric ratios of TS-100 to water are between 1:500 and 1:1,000. For this range of ratios, obtain ZOD permission for surfactant (anionic and nonionic) by way of Rule 62-520.310(8)(c), F.A.C., as described in paragraph four (4) above. Per a Division of Waste Management calculation, the dilution ratio at which surfactant ZOD permission is no longer necessary for TS-100 is 1: 414,359, which is so dilute that it is unlikely to ever be injected at that concentration.

   b) **TerraCleanse-1200** (TC-1200): The typical injection (or re-injection) volumetric ratios of TC-1200 to water are between 1:750 and 1:1,500. For this range of ratios, obtain ZOD permission for surfactant (anionic and nonionic) by way of Rule 62-520.310(8)(c), F.A.C., as described in paragraph four (4) above. Per a Division of Waste Management calculation, the dilution ratio at which surfactant ZOD permission is no longer necessary for TS-1200 is 1: 922,319, which is so dilute that it is unlikely to ever be injected at that concentration.

   c) **TerraCleanse-1200nzvi** (TC-1200nzvi): The typical injection (or re-injection) volumetric ratio of TC-1200nzvi to water is 1:500. For this ratio, obtain ZOD permission for surfactant (nonionic) by way of Rule 62-520.310(8)(c), F.A.C., as described in paragraph four (4) above. Per a Division of Waste Management calculation, the dilution ratio at which surfactant ZOD permission is no longer necessary for TS-1200nzvi is 1: 2,428. The Division of Waste Management has done additional calculations for TC-1200nzvi, in order to have information ready for users and reviewers in the future, should there ever be a need to inject TC-1200nzvi at higher concentrations. At a volumetric ratio of 1:57 TC-1200nzvi to water in the fluid to be injected, it will be necessary to obtain ZOD permission by way of Rule 62-520.310(8)(c), F.A.C., for iron and surfactant. As for ratio of 1:2, it will be necessary to obtain permission by way of that same rule for ammoniacal nitrogen, iron, and surfactant. As for the heavy metal impurities arsenic, cadmium, and lead that could be present in the nutrient component of TC-1200nzvi, there is no need to seek ZOD permission since the concentration of each of these impurities in TC-1200, as shipped by TerraHydroChem, Inc., is already less than the maximum allowable concentration allowed by Florida Drinking Water Standards I Chapter 62-550, F.A.C.

   d) **TC-nZVI** (Sodium Bicarbonate): When the concentration of TC-nZVI in the fluid to be injected or re-injected is greater than or equal to 546 milligrams per liter (mg/L), which is equivalent to 0.0546 percent by weight, it will be necessary to seek ZOD permission by way of Rule 62-

520.310(8)(c), F.A.C, for sodium, total dissolved solids, and pH. At sites where TC-1200nzvi has already been introduced to the subsurface during an earlier phase of treatment, the iron already in the subsurface can serve as a catalyst to produce a Fenton reaction. But if a catalyst other than the iron in TC-1200nzvi will be used to activate the sodium bicarbonate, then the site-specific Remedial Action Plan shall indicate the following: the concentration of the catalyst in the fluid to be injected or re-injected, the complete chemical composition of the catalyst, and an evaluation of whether or not ZOD permission is needed for the specified concentration of catalyst in the fluid to be injected or re-injected.

e) **TerrOx** (Zero-Valent Iron): When the concentration of TerrOx in the fluid to be injected or re-injected is greater than or equal to 0.3 milligrams per liter (mg/L), which is equivalent to 0.00003 percent by weight, it will be necessary to seek ZOD permission by way of Rule 62-520.310(8)(c), F.A.C., for iron. As for the diatomic nitrogen that the injection system also uses when TerrOx is injected, no ZOD is needed. But if other chemicals will be injected along with the zero-valent iron, then the site-specific Remediation Action Plan shall indicate the following: the concentration of the chemical in the fluid to be injected or re-injected, the complete chemical compositions of the chemical, and an evaluation of whether or not ZOD permission is needed for the specified concentration of that chemical in the fluid to be injected or re-injected.

f) For the ZOD parameters ammonia, iron, pH, sodium, surfactant, and total dissolved solids (TDS) reviewers of Remedial Action Plans, when filling out the UIC Notification memorandum, should check the box labelled below as follows:
"☑ *ZOD permission by rule* 62-520.310(8)(c), F.A.C., for *reagent chemical species and/or parameter(s) in the fluid to be injected (or re-injected) that exceed groundwater standards…",*

6. Required UIC ZOD compliance monitoring or the five types of injection fluids discussed above, quarterly monitoring of groundwater should suffice in most cases for the chemicals and parameters that require ZOD permission. The current groundwater regulatory values for the chemicals and parameters listed above are as follows: ammonia = 2.8 mg/L, iron = 0.3 mg/L, pH = 6.5-8.5, sodium = 160 mg/L, surfactant = 0.5 mg/L, and total dissolved solids = 500 mg/L.

   Note: Currently ammonia is identified in Chapter 62-777, F.A.C., as a "minimum criteria systemic toxicant" and it has a Groundwater Cleanup Target Level (GCTL) of 2.8 mg/L. However, the oral reference dose upon which this number is based has been withdrawn from the U.S. Environmental Agency's (EPA) Integrated Risk Information System (IRIS) database. Therefore, the FDEP has calculated an alternative groundwater cleanup target level in accordance with Chapter 62-780, F.A.C. This Alternative Groundwater Cleanup Target Level (AGCTL) calculation is attached as Enclosure 4. The Department recommends using the referenced AGCTL for ammonia.

   Upon expiration of the time-period granted for the ZOD, the concentration of each must meet its respective groundwater standard, or its natural-occurring backgrounds value at the specific cleanup site, whichever is less stringent. Conditional closure with exceedances of the secondary standard (or background) is also allowable provided the closure criteria of Chapter 62-780.680, F.A.C. are met. Note that such conditional closure may require a modification of the size or duration of the ZOD. This modification must be approved in an enforceable order of the department, such as

a conditional Site Rehabilitation Completion Order.

7. Analytical method for surfactants: Per Chapter 62-550, F.A.C., Standard Method 5540 (SM 5540) can be used to determine the concentrations of surfactants in water samples. Method SM 5540 C is for the measurement of anionic surfactant concentrations, and method SM 5540 D is for the measurement of nonionic surfactant concentrations.

8. Utilization of wells: If a remediation site happens to have an abundance of monitoring wells, then the Division of Waste Management has no objection to the use of some wells for the injection (or re-injection) of TerraHydroChem™ products if the wells are suitable for the purpose. However, no "designated" monitoring well, dedicated to the tracking of remediation progress (by sampling) shall be used to apply TerraHydroChem™ products. This will avoid a premature conclusion that the entire site meets cleanup goals. By making sure that designated tracking wells are not used for treatment, there will be more assurance that the treatment process has permeated the entire site and that it did not remain localized to the area immediately surrounding each injection well.

9. Three categories of groundwater monitoring:

   a. Active remediation monitoring for a cleanup site's contaminants of concern: During the period of active remediation, groundwater shall be monitored in accordance with the requirements set forth in Section 62-780.700, F.A.C.

   b. Post Active Remediation Monitoring for a cleanup site's contaminants of concern: At least one (1) year of quarterly post remediation groundwater monitoring for the contaminants of concern shall be conducted at a minimum of two (2) wells: one located in the area of highest contamination, the other at the downgradient edge of the contamination plume, pursuant to Section 62-780.750, F.A.C.

   c. Monitoring of the UIC zone of discharge: For TerraHydroChem™ products (TS-100, TC-1200, TC-1200nzvi, TerrOx, TC-nZVI), in order to comply with Rule 62-520.310(8)(c), F.A.C., monitor the ZOD for ammonia, iron, pH, sodium, surfactant, and TDS as discussed in paragraph six (6) above.

13. Injection operations:

1. Avoidance of migration: For injection-type in-situ aquifer remediation projects, injection of TerraHydroChem™ products shall be performed in such a way and at such a rate and volume that no migration of either the TerraHydroChem™ products or the contaminants of concern in the aquifer or surface water results, pursuant to Rule 62-528.630(3), F.A.C.

2. Underground Injection Control operating permit: Although an operating permit is not required for aquifer remediation wells pursuant to Rule 62-528.640(1)(b), and 62-528.640(1)(c), F.A.C., since no movement of the contamination plume is expected to accompany the treatment process, the Department requests that the information items listed in Rule 62-528.640(1)(b), F.A.C., be considered and included in Remedial Action Plan proposals as a matter of good and thorough design practice. Briefly summarized, they are: quality of water in the aquifer, quality of the injected fluid, existing and potential uses of the affected aquifer, and well construction details.

14. Abandonment of wells: Upon issuance of a Site Rehabilitation Completion Order or a declaration of "No Further Action", injection wells shall be abandoned pursuant to Section 62-528.645, F.A.C. The Underground Injection Control Section of the Department shall be notified so that the injection wells can be removed from the inventory-tracking list.

15. Open-pit application: There is no objection to the introduction of TerraHydroChem™ products to an open excavation pit in which the groundwater has been exposed. Open-pit application is not injection, and it is not necessary to notify the Underground Injection Control Section, but this should not be construed as carte blanche to introduce to the pit any substance at any concentration with no regard to potential toxicological effects. The Division of Waste Management therefore recommends that the groundwater in the area of the pit be monitored for the same zone of discharge parameters that would have been monitored (if any) had the application actually been an injection.

1. Manufacturer/Distributer: TerraHydroChem™, Inc. – http://www.terrahydrochem.com

2. Description: Per the manufacturer's description:

a) Injection (or re-injection) of the TerraHydroChem™ products can be utilized through the Star System. Star System is a trailer-mounted treatment and delivery system with a flexible equipment configuration. Although it can be used for direct loop-type re-injections in which recovered groundwater is treated ex situ by process equipment and amended with remediation reagents prior to re-injection in order to continue the treatment in situ.

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b) Free product: If a high level of free product is present at a cleanup site, then the Star System makes use of an oil/water separator (OWS) as the first- step in its aboveground treatment part of the process.

c) Pre-treatment: The Star System actually makes use of two equipment trailers. When a high level of free product is present at a site, a pre-treatment trailer is used, containing an OWS, to remove and collect bulk free product from recovered groundwater, before the free product can travel any further through the Star System equipment train.

The pre-treatment trailer also contains a 500-gallon sludge treatment tank for the batch treatment of any sludge that may settle in the OWS. TerraCleanse-1200nzvi (TC-1200nzvi) is added to each batch of sludge in the volumetric ratio of approximately 1:1,000. Water exiting the OWS and the sludge treatment tank is then passed through a set of organoclay filters before it is sent along to the injection trailer, where it is amended with the appropriate TerraHydroChem™ product prior to re-injection. Water passed from the pre-treatment trailer to the injection trailer does not contain residual TerraCleanse-1200nzvi (TC-1200nzvi).

d) Air: The Star System equipment trailers contain air compressors. On the pre-treatment trailer, the batch treatment sludge tank is air-agitated. On the injection trailer, compressed air is used to drive a pneumatic pump, and to provide oxygen for aerobic treatment processes. When the Star System needs to introduce air to the subsurface for an aerobic process, the compressed air and the fluid to be injected or re-injected are combined in a mixing manifold (while both are still aboveground) and then directed to the subsurface.

e) Nitrogen: The Star System injection trailer also carries a supply of pure diatomic nitrogen (N_2) that is used when zero-valent iron (a reducing agent) is being injected. It serves to prevent the zero-valent iron from oxidizing before it has a chance to reach its target contaminants in the subsurface.

ENCLOSURE 4

UF UNIVERSITY of FLORIDA

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September 1, 2015

Brian Dougherty, PhD
Office of District and Business Support
Division of Waste Management
Florida Department of Environmental Protection
2600 Blair Stone Road
Tallahassee, FL 32399-2400

Re: Calculation of an alternative groundwater cleanup target level for un-ionized ammonia

Dear Dr. Dougherty:

At your request, we have calculated alternative groundwater cleanup target levels (AGCTL) for total ammonia based on water temperature and pH. As you know, calculation of an AGCTL necessitates consideration of exposure from oral, dermal, and inhalation pathways (Chapter 62-780, FAC). The GCTL equation promulgated in Chapter 62-777, FAC calculates a criterion for groundwater based on the oral route, but does not consider other routes of exposure. The FDEP has not specified a preferred methodology for calculating exposure for the inhalation and dermal routes from groundwater. Therefore, to aid our calculation, we utilized the USEPA regional screening level (RSL) tap water equation, which includes exposure from the inhalation and dermal routes.

We reviewed current toxicity values available for ammonia using the hierarchy of toxicity sources promulgated in Chapter 62-780, FAC. No oral reference dose (RfD_o) is currently available for ammonia. An inhalation reference concentration (RfC) of 0.1 mg/m^3 is available from the USEPA's IRIS database.[1] This value was based on a lack of decreased pulmonary function or changes in subjective symptomatology in humans (USEPA, 1991). As this effect is route specific to inhalation, an RfD_o cannot be extrapolated from the RfC. Without an oral reference dose, the toxicity from exposure by the oral and dermal routes cannot be estimated. While it is possible for ammonia to cause direct irritation of the skin due to its alkaline properties, quantitative data are lacking and it is not possible to calculate with any certainty the concentration of ammonia in groundwater that would cause irritation from direct contact (ATSDR, 2004). Therefore, the AGCTL was calculated based on inhalation exposure to ammonia volatilized from groundwater.

[1] The USEPA has recently proposed an updated RfC of 0.3 mg/m^3, but this has not been approved or posted on IRIS. The time frame for completing this update is unknown.

To calculate an AGCTL for total ammonia, it was first necessary to estimate the risk-based concentration of un-ionized ammonia that would be of concern (since this is the fraction that will volatilize). We utilized the USEPA equation for tap water for non-carcinogenic effects by the inhalation route to calculate a risk-based concentration for un-ionized ammonia (Figure 1). Calculation of an AGCTL under Chapter 62-780, FAC also requires the consideration of sensitive sub-populations. Because ammonia is a non-carcinogen, children are the appropriate receptor of concern.

Figure 1: USEPA RSL equation for inhalation exposure from tap water for a non-carcinogen

$$NH_3\left(\frac{\mu g}{L}\right) = \frac{THQ \times AT \times CF}{EF \times ED \times ET \times \left(\frac{1\,day}{24\,hours}\right) \times \left(\frac{1}{RfC}\right) \times K}$$

Parameter	Definition (units)	Default Value
NH_3	un-ionized ammonia (µg/L)	--
THQ	target hazard quotient	1
AT	child averaging time (days)	2190
CF	conversion factor (µg/mg)	1000
EF	exposure frequency (d/y)	350
ED	exposure duration (years)	6
ET	resident water exposure time (hours/day)	24
RfC	inhalation reference concentration (mg/m^3)	0.1
K	Andelman Volatilization Factor (L/m^3)	0.5

The risk-based concentration of un-ionized ammonia was calculated as:

$$NH_3\left(\frac{\mu g}{L}\right) = \frac{1 \times 2190 \times 1000}{350 \times 6 \times 24 \times \left(\frac{1\,day}{24\,hours}\right) \times \left(\frac{1}{0.1}\right) \times 0.5}$$

$$NH_3\left(\frac{\mu g}{L}\right) = 208.57\ (rounded\ to\ 210)$$

In groundwater, ammonia concentrations are reported as total ammonia. The reported value is the sum of both the un-ionized (NH_3) and ionized (NH_4^+) forms. The FDEP has a manual for the calculation of un-ionized ammonia based on total ammonia concentrations in fresh water, pH, and temperature (FDEP, 2001). The concentration of unionized ammonia can be calculated using the FDEP Unionized Ammonia Calculator v1.2 or using the equations below. Based on the methodology presented in the FDEP manual, the mole fraction of un-ionized ammonia is calculated using the following equations:

$$f = 1/(10^{(pKa-pH)} + 1)$$

$$pKa = 0.0901821 + 2729.92/T_k$$

$$T_k = °C + 273.2$$

where:
f = the mole fraction of un-ionized ammonia
T_k = temperature in degrees Kelvin
°C = temperature in degrees Celsius

The mole fraction of un-ionized ammonia is used to determine the concentration of un-ionized ammonia using the following equation:

$$Ammonia_{total} \times f \times \left(\frac{17}{14}\right) = NH_3$$

where:
$Ammonia_{total}$ = total ammonia (μg/L)
NH_3 = un-ionized ammonia (μg/L)

Table 1 (attached) lists AGCTLs for total ammonia based on a range of common pH values and temperatures for Florida groundwater. The AGCTLs listed in Table 1 do not consider organoleptic effects. The odor threshold for total ammonia in tap water is 1,500 μg/L and for taste is 35,000 μg/L (ATSDR, 2004). Based on Table 1, the risk-based concentration of total ammonia will likely exceed the odor threshold and will exceed the taste threshold at pH less than 7.0.

Because the concentration of un-ionized ammonia increases with water temperature, showering/bathing represents an acute exposure scenario where residents are exposed for short periods of time to relatively higher concentrations of un-ionized ammonia in air. We could not find any published data regarding the average temperature of water used for showering. However, 120°F (48.9°C) is considered a safe hot water temperature (Shields et al., 2013). Exposure to 48.9°C water takes 10 minutes to cause a serious burn and therefore can be used as the maximum likely shower temperature (Shields et al., 2013). Using the equations above, at water temperature of 48.9°C and a pH of 7.5 (chosen because it produces the largest fraction of un-ionized ammonia), the fraction of un-ionized ammonia available for inhalation would be 7.9%. The maximum airborne concentration of ammonia below which it is believed nearly all individuals could be exposed for up to one hour without experiencing anything other than mild, transient effects or without perceiving a defined odor is 25 ppm (AIHA, 2015). Using maximum allowable air concentration of 25 ppm for un-ionized ammonia and a water temperature of 48.9°C results in an acute AGCTL of 260,000 μg/L. Therefore, the AGCTLs in Table 1 were limited to a maximum concentration of 260,000 μg/L to protect against acute exposures.

Please let us know if you have any questions regarding the derivation of this AGCTL.

Sincerely,

Leah D. Stuchal, Ph.D.

Hannah M. Neeley, MPH

Stephen M. Roberts, Ph.D.

References:

AIHA (2015) *2015 ERPG Levels.* American Industrial Hygiene Association, Emergency Response Planning Guidelines, Falls Church, VA.

ATSDR (2004) *Toxicological Profile for Ammonia.* US Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

FDEP (2001) *Calculation of Un-Ionized Ammonia in Fresh Water.* Florida Department of Environmental Protection, Chemistry Laboratory Methods Manual, Tallahassee.

Shields, WC, McDonald, E, Frattaroli, S, Zhu, J, Perry, EC, and Gielen, AC. (2013) Still too hot: Examination of water temperature and water heater characteristics 24 years after manufacturers adopt voluntary temperature setting. *J Burn Care Res.* 34(2): 281-287.

USEPA (1991) *Ammonia (CASRN 7664-41-7).* United States Environmental Protection Agency, Integrated Risk Information System, http://www.epa.gov/iris/subst/0422.htm

Table 1 – AGCTLs in µg/L (ppb) for total ammonia based on a range of common pH and temperatures for Florida groundwater

pH	20°C	21°C	22°C	23°C	24°C	25°C	26°C	27°C	28°C	29°C	30°C
5.5	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*
5.6	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*
5.7	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*
5.8	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*
5.9	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*
6.0	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	260,000*	250,000	230,000	210,000
6.1	260,000*	260,000*	260,000*	260,000*	260,000*	240,000	230,000	210,000	200,000	180,000	170,000
6.2	260,000*	260,000*	240,000	220,000	210,000	190,000	180,000	170,000	160,000	150,000	130,000
6.3	220,000	200,000	190,000	180,000	160,000	150,000	140,000	130,000	120,000	120,000	110,000
6.4	170,000	160,000	150,000	140,000	130,000	120,000	110,000	110,000	98,000	92,000	86,000
6.5	140,000	130,000	120,000	110,000	100,000	96,000	90,000	84,000	78,000	73,000	68,000
6.6	110,000	100,000	95,000	88,000	82,000	77,000	71,000	67,000	62,000	58,000	54,000
6.7	87,000	81,000	75,000	70,000	65,000	61,000	57,000	53,000	49,000	46,000	43,000
6.8	69,000	64,000	60,000	56,000	52,000	48,000	45,000	42,000	39,000	37,000	34,000
6.9	55,000	51,000	48,000	44,000	41,000	38,000	36,000	33,000	31,000	29,000	27,000
7.0	44,000	41,000	38,000	35,000	33,000	31,000	28,000	27,000	25,000	23,000	22,000
7.1	35,000	32,000	30,000	28,000	26,000	24,000	23,000	21,000	20,000	18,000	17,000
7.2	28,000	26,000	24,000	22,000	21,000	19,000	18,000	17,000	16,000	15,000	14,000
7.3	22,000	20,000	19,000	18,000	17,000	15,000	14,000	13,000	13,000	12,000	11,000
7.4	18,000	16,000	15,000	14,000	13,000	12,000	11,000	11,000	10,000	9,300	8,700
7.5	14,000	13,000	12,000	11,000	10,000	9,800	9,200	8,500	8,000	7,500	7,000

* - acute exposure AGCTL

AGCTLs were calculated using an f value rounded to 5 significant digits and an un-ionized ammonia concentration of 210 µg/L