Petroleum Cleanup Program

REMEDIAL ACTION PLAN GUIDELINES

BUREAU OF PETROLEUM STORAGE SYSTEMS

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Chemicals may be added as liquids, solids, slurries or gases for in situ remediation of petroleum and other contaminants in the vadose zone and aquifer of contaminated sites. They may be used to destroy contaminants by direct chemical reaction, or through biological processes that they induce or enhance by supplying nutrients, and oxygen in the case of aerobic biodegradations. Some examples of the types of chemicals that may be used for remediation purposes are oxidizers, reducing agents, catalysts, surfactants, emulsifiers, co-solvents, and nutrients in the case of biological processes. Non-indigenous microorganisms alone are generally not classified as chemical additives, but when used as in situ bioaugmentation, consideration should be given to them, just as consideration would be given to chemicals with respect to applicable Underground Injection Control requirements and groundwater criteria. The methods of introducing chemicals to a remediation site include but are not necessarily limited to direct injection, re-injection, dispersion from a retrievable sock or cartridge, infiltration, tilling, and addition to an excavation pit.

This guidance applies to direct injection, re-injection, and all methods of application for in situ remediation chemicals, and closed-loop re-injection or reinfiltration of partially treated remediation system effluent that still contains petroleum chemicals or other contaminants of concern at concentrations in excess of their groundwater standards. It was originally written for petroleum cleanups conducted pursuant to Chapter 62-770, Florida Administrative Code (F.A.C.), which is the jurisdiction of the Bureau of Petroleum Storage Systems, a subsection of the Division of Waste Management, but the advice that it offers in regard to compliance with Underground Injection Control regulations and groundwater criteria is also applicable to the cleanup of aquifers contaminated by hazardous wastes within the jurisdictions of the Bureau of Waste Cleanup and other member bureaus of the Division of Waste Management.

This guidance does not apply to disposal, via injection, of remediation system effluent that has been fully treated to meet primary and secondary groundwater standards, and minimum groundwater criteria. For guidance on that topic, see BPSS-8, "Effluent Disposal via Injection Well".

1. **Applicable regulations.** Portions of the following chapters of the Florida Administrative Code may be applicable to the use of in situ chemical additives that are injected or re-injected into an aquifer, sprayed, or broadcasting of powder or poured into the exposed groundwater in an excavation pit, or introduced to the aquifer at a remediation site by some other method such as an infiltration gallery or trench: Chapter 62-550, F.A.C., primary and secondary water quality standards; Chapter 62-520, F.A.C., groundwater classes, standards, and minimum criteria; Chapter 62-522, F.A.C., groundwater permitting and monitoring requirements; Chapter 62-528, F.A.C., underground injection control (UIC), particularly sections pertaining to Class V, Group 4 aquifer remediation wells; and the minimum groundwater criteria and contaminant cleanup target levels of Chapter 62-777, F.A.C. These chapters are currently located at web page www.dep.state.fl.us/legal/Rules/rulelistnum.htm

2. **Classification of injection wells.** Injection wells for aquifer remediation projects are classified by Rule 62-528.600(2)(d), F.A.C., as Class V, Group 4 aquifer remediation wells, provided the substances they inject do not exceed the drinking water standards set forth in Chapter 62-550, F.A.C. (See section 5 below for permitting a Zone of Discharge for injection wells used for aquifer remediation when water quality standards of the injected fluid will be exceeded)

3. **Criteria for injection.** In addition to the requirement that chemical additives injected into an aquifer meet the primary and secondary drinking water standards set forth in Chapter 62-550, F.A.C., they must also meet the minimum criteria for groundwater set forth in Section 62-520.400, F.A.C., and Chapter 62-777, F.A.C. The minimum criteria of section 62-520.400, F.A.C., require that groundwater be free from substances that are harmful to plants, animals, and organisms, and free from substances that are carcinogenic, mutagenic, teratogenic or toxic to human beings.

   Regardless of whether a fluid (or non-liquid substance such as dry powder in remediation "socks" placed in remediation wells) is introduced to the subsurface as a "one-time" direct injection, or as part of a re-injection loop, it is required by Chapter 62-528, F.A.C., that the quality of the fluid be compared to the primary and secondary drinking water standards, and the minimum criteria for groundwater before it is injected (i.e., before it is diluted by the receiving groundwater). If the chemical composition of the fluid does not meet these requirements, then permission for a temporary injection zone of discharge must be sought for the parameters that do not meet their criteria. (Procedures for establishing a permitted Zone of Discharge described in section 5 below)

4. **Definition of Injection Well:** The definition of an injection well under Chapter 62-528, F.A.C., is - *"Well" means a bored, drilled or driven shaft, or a dug hole, which has a*

depth greater than the diameter of the largest surface dimension; or, an improved sinkhole; or, a subsurface fluid distribution system. For the purpose of use of chemical or biological remediation products or for recirculation of partially treated water for the beneficial remediation of a contaminated site, the phrase "subsurface fluid distribution system" is intended to include infiltration galleries, infiltration trenches, pouring of remediation product fluid or broadcasting remediation products in powder form in an open excavation, provided these activities are first proposed to the Department in a Remedial Action Plan which is approved by the Department before the remediation is conducted and the other requirements of applicable Department rules and this guidance are followed. Therefore, the remainder of this guidance document concerning permitting a temporary Zone of Discharge, Zone of Discharge monitoring, approval procedures, etc. is applicable to these other methods of application of remediation products or recirculation of partially treated groundwater in addition to applying these fluids with conventional injection wells.

However, at the present time the reporting of Underground Injection Control (UIC) information to the Department's UIC Section only applies when injection wells are used which have a depth greater than the diameter of the largest surface dimension. For example, under this criteria, an infiltration gallery for recirculation of partially treated water or the application of remediation products to the groundwater in an open excavation may be allowed a zone of discharge provided the criteria described in this guidance document are met, but these type of applications will not normally be reportable to the FDEP UIC Section as an injection well. However, if a contaminated soil excavation is performed with Large Diameter Auger excavation into the saturated zone and remediation products are applied to the groundwater in the bottom of the boring before backfilling the LDA boring, this would be considered an injection well event that is reportable to the UIC section.

5. **Two ways of permitting a temporary Zone of Discharge (ZOD).** If a fluid to be injected into an aquifer for remediation purposes does not meet the criteria for injection, then it will be necessary to first obtain permission for a temporary injection zone of discharge. The zone will be permitted either **by Rule** 62-520.310(8)(c), F.A.C., **or by variance**, depending on the type of injection system, and whether the chemical species to be injected are prime constituents of the reagents needed to remediate site contaminants, or primary or secondary drinking water contaminants, or minimum groundwater criteria contaminants.

   a. **ZOD by Rule.** On August 27, 2001, Rule 62-522.300(2)(c), F.A.C., became effective, making it possible in most (though not all) cases to obtain permission by rule, rather than by variance, for a temporary injection zone of discharge for aquifer remediation purposes. It should be noted that, as of July 12, 2009, Rule 62-522.300(2)(c), F.A.C., was relocated to Chapter 62-520 of the Florida Administrative Code and renumbered as Rule 62-520.310(8)(c), F.A.C., without any changes to its wording.

The actual wording of Rule 62-520.310(8)(c), F.A.C., which applies to Department-approved aquifer remediation projects that use Class V, Group 4, injection wells is as follows: *"A zone of discharge shall be allowed for primary standards for ground water for closed-loop re-injection systems and for the prime constituents of the reagents used to remediate site contaminants, and for the secondary standards for ground water, as specified in a Department-approved remedial action plan that addresses the duration and size of the zone of discharge, and ground water monitoring requirements".*

The rule is dissected and explained below.

"...for primary standards for ground water for closed-loop re-injection systems..." A closed-loop is one in which fluid recirculates; for example: a recirculating, re-injection type groundwater treatment system that contains an air stripper that removes some but not necessarily all of the groundwater's contaminants. Nothing is added to the loop, and (with the exception of the contaminants) nothing is removed. The intent of this part of the rule is to permit a temporary zone of discharge for the re-injection of partially treated site contaminants that may be re-injected at concentrations in excess of their groundwater standards. For example: benzene, a primary groundwater contaminant, re-injected in excess of 1 part per billion (ppb); or vinyl chloride, another primary groundwater contaminant, re-injected in excess of 1 ppb. Closed-loop means that there is hydraulic control of groundwater in the area of injection such that virtually all of the injected fluid containing chemicals which exceed groundwater standards at the point of injection will be recovered again by the groundwater recovery wells. It is the responsibility of the preparer of a RAP proposing closed loop recirculation to design the system to meet this objective and to also operate the system in a manner consistent with this objective.

"...and for the prime constituents of the reagents used to remediate site contaminants,..." This portion of the rule permits a temporary injection zone of discharge for the reagents used to remediate site contaminants, regardless of whether those reagents are introduced to the aquifer as a direct injection, or indirectly by way of a recirculating re-injection-type system. The key words in this portion of the rule are "prime constituents". For example: The two prime constituents of sodium permanganate, a reagent used to chemically oxidize contaminants, are sodium and the permanganate ion. Sodium happens to be a state primary groundwater contaminant, but since it is a prime constituent of the reagent needed to remediate site contaminants, it is permitted a temporary zone of discharge by the rule.

The rule, however, does not permit a zone of discharge to other primary groundwater contaminants that may be present as impurities, in concentrations that exceed their primary groundwater standards in the sodium permanganate fluid to be injected; for example: heavy metal impurities such as cadmium, chromium,

mercury, lead, etc. These impurities are not prime constituents of sodium permanganate; they are not reagents that are needed to remediate the contaminants at a site; and they are not permitted a temporary injection zone of discharge by this portion of the rule, or any other portion of it. For primary groundwater contaminant impurities of this type, a zone of discharge can only be permitted by variance. A zone of discharge variance is also needed for the injection of potassium permanganate, which, like sodium permanganate, contains a number of heavy metal impurities that are classified as primary groundwater contaminants. The only exception to the need for a variance would be injection of such a dilute permanganate solution that each heavy metal impurity in the fluid to be injected does not exceed its respective primary drinking water maximum contaminant level.

For secondary groundwater contaminants, however, regardless of whether they are prime constituents of the reagents needed to remediate contaminants, or whether they are impurities, this portion of the rule permits a temporary injection zone of discharge.

Minimum groundwater criteria contaminants. Rule 62-520.310(8)(c), F.A.C., does not specifically address minimum groundwater criteria contaminants, but Section 62-520.400, F.A.C., establishes minimum criteria in general, and Chapter 62-777, F.A.C., establishes minimum groundwater criteria for specific chemicals. However, for purposes of this discussion in regard to Rule 62-520.310(8)(c), F.A.C., it may be more helpful -- as a working definition -- to consider a minimum groundwater criteria contaminant to be any contaminant that is neither a primary nor a secondary groundwater contaminant.

If a minimum groundwater criteria contaminant happens to be a prime constituent of the reagents used to remediate a site, then a temporary injection zone of discharge is permitted by Rule 62-520.310(8)(c), F.A.C. For example: The Florida Department of Environmental Protection's Underground Injection Control Program, on April 7, 2005, in regard to case number OGC 05-0356, indicated that soybean oil (which is essentially total recoverable petroleum hydrocarbons), and polysorbate 80 (a surfactant), were prime constituents of the reagents of a product used to remediate site contaminants, and as such were permitted a zone of discharge by the rule. Likewise, a temporary ZOD would be permitted by this rule for ammonia nitrogen, a common prime constituent of bioremediation formulas used to remediate site contaminants. Ammonia nitrogen is classified as a minimum groundwater criteria contaminant, and is listed in Chapter 62-777, F.A.C., with a maximum allowable groundwater concentration of 2.8 milligrams per liter.

The Bureau of Petroleum Storage Systems, however, would like to indicate that those who inject remediation products into an aquifer should not consider it to be a carte blanche allowance to leave a chemical, which is a component of the

remediation product formulation and does not have a primary or secondary standard or otherwise have a CTL in Chapter 62-777, in the groundwater at any concentration when it is a minimum groundwater criteria contaminant which happens to be a prime constituent of the reagent that is injected to remediate contaminants at a site. If it cannot be established to a reasonable degree of satisfaction that the substance is toxicologically benign to humans and the environment, then it may be necessary to determine the maximum allowable residual concentration of the substance that can safely remain in the groundwater upon completion of the cleanup project. The Department, with the assistance of the University of Florida's Center for Environmental and Human Toxicology, can establish groundwater criteria for substances of toxicological concern when no criteria exists, but the financial and technical onus shall be on the user of the substance to identify or develop a laboratory analytical method to measure the residual concentrations in groundwater samples after a criterion has been developed.

"...remedial action plan that addresses the duration and size of the zone of discharge...". The duration (time period) and size (dimensions) of the temporary injection ZOD are relatively straightforward and easy to understand. In regard to duration, a Department-approved Remedial Action Plan must include in its groundwater monitoring schedule any chemical species (whether it be a primary, secondary, or minimum groundwater criteria contaminant) whose concentration in the fluid to be injected does not meet its groundwater standard. In some cases there may also be by-products of the chemical species of the remediation product that are produced by chemical or biological reactions, and in such case the RAP's proposed monitoring schedule must also include monitoring of these by-products to be conducted to verify the groundwater quality returns to groundwater standards by the conclusion of site rehabilitation. For remediation products which have been issued a product specific variance because the product formulation contains impurities which are not "prime constituents" of the remediation product and will exceed primary standards at the point of injection, the variance will specify the duration of time for which groundwater standards may be exceeded.

The number of groundwater monitoring wells to be sampled for the chemical species, and the frequency of their sampling should be determined on a site-specific basis. In most cases (for example a relatively small zone with an areal extent of ¼-acre or less) the sampling of two (2) wells on a quarterly basis should suffice, with one well being located at approximately the center of the injection zone, and the other located just beyond the downgradient edge of the zone to serve as a sentry for undesirable migration. The monitoring of a chemical species associated with the reagents used to remediate site contaminants (or by-products that result from chemical reaction or biodegradation processes) may cease when it has been demonstrated with reasonable assurance that their concentrations meet their groundwater standards or natural-occurring background level at a remediation site, whichever is less stringent. For guidance on

establishment of naturally occurring background concentrations in groundwater, the Division of Waste Management guidance document, *Guidance for Comparing Background and Site Chemical Concentrations in Groundwater* which can be found at http://www.dep.state.fl.us/waste/quick_topics/publications/wc/DraftGroundwaterBackgroundGuidance.pdf should be considered.

As a minimum, the verification monitoring that chemicals which were part of the remediation product formulation are no longer present in excess of groundwater standards should meet the same requirements as for Natural Attenuation Monitoring of contamination following active remedial action as indicated in the Department's cleanup rules. That is, a minimum of 4 quarters of monitoring is necessary and groundwater standards (or naturally occurring background levels) should not be exceeded for the last two consecutive quarters. This monitoring of the effects of the remediation product may be on a separate track from the monitoring of the chemicals which were the target of remediation, in that it might be determined that the effects of the remediation product are no longer causing exceedences of groundwater standards such that the monitoring of those parameters may cease after four quarters; but monitoring of other chemicals which were the target of remedial action must continue because those chemicals still exceed groundwater criteria. Alternatively, it might be concluded that the monitoring of the chemicals which were the target of remediation have met the rule-based Natural Attenuation Monitoring or Post Active Remediation Monitoring requirements to qualify the discharge for No Further Action such that monitoring of those chemicals can be concluded; however, monitoring of chemicals which were components of the remediation product would need to continue if they are continuing to cause exceedence of groundwater standards. In this case the site cannot qualify for a determination by the Department of Site Rehabilitation Completion unless both the target chemicals of remediation and the effects of the remediation products are demonstrated to meet groundwater standard criteria.

b. **ZOD by Variance.** It will be necessary to petition the Department, pursuant to Chapter 120, Florida Statutes, for a variance that permits a temporary injection zone of discharge when the composition of a fluid to be injected for aquifer remediation purposes is such that a temporary ZOD cannot be permitted by Rule 62-520.310(8)(c), F.A.C. For example: the heavy metal impurities that may be present in sodium permanganate, as discussed in *Section 5a* above. These impurities are classified as primary drinking water contaminants; they are not prime constituents of the sodium permanganate reagent that is used to remediate a site's contaminants; and as such they are not permitted a temporary ZOD by Rule 62-520.310(8)(c), F.A.C. Instructions on how to petition for a variance that permits a temporary injection zone of discharge for aquifer remediation purposes are located at Bureau of Petroleum Storage Systems web page www.dep.state.fl.us/waste/categories/pcp/pages/innovative.htm. Whether the

petitioner has met all of the variance requirements is determined by the Department on a case-by-case basis. An Internet link to copies of all variances granted to date is also available at this same web page.

c. **ZOD by combination of rule and variance**. If the chemical composition of a fluid to be injected for aquifer remediation purposes is such that some of the chemical species are permitted a zone of discharge by Rule 62-520.310(8)(c), F.A.C., and that others require a variance, then the ZOD must be permitted by a combination of the two regulatory mechanisms. Those who submit variance petitions for such a situation should indicate in their petition which chemical species are in need of a variance, and which are covered by Rule 62-520.310(8)(c), F.A.C.

6. **ZOD parameters for closed-loop re-injection.** For the purposes of this discussion, a re-injection loop for in situ aquifer remediation shall be an operation in which groundwater containing a site's contaminants of concern is recovered (brought to the surface) continuously, intermittently or in batches, and treated either partially or fully by physical, chemical or biological methods, or a combination of them, and may also be amended by chemical or biological additives prior to re-injection into the aquifer.

For aquifer remediation projects involving only one-time direct injections, it is relatively easy to know beforehand, and with certainty, the complete chemical composition of the fluid to be injected, and therefore relatively easy to identify which parameters, if any, must seek permission for a temporary injection ZOD. But in the case of a fluid to be re-injected on a continuous or intermittent basis, it may not be so easy to know with certainty, at all times, its complete chemical composition with respect to the ingredients of partially-consumed chemical additives and/or partially-treated site contaminants. Therefore, in the case of re-injection, it may at times be necessary to make some simplifying assumptions to conservatively identify (i.e., overestimate) the number of chemical species that might be in need of a temporary zone of discharge.

There are a number of factors that can cause variations in the chemical composition of a re-injection fluid during the course of an aquifer remediation project; for example: whether the petroleum or other contaminants of concern have been fully, partially, or not at all treated by an aboveground treatment system prior to re-injection; whether a metering pump continuously adds a small volume of fresh chemicals prior to re-injection, or whether the addition of fresh chemicals occurs only periodically as a large batch; and whether the chemicals are totally consumed by the time they have completed their travel through the underground portion of the re-injection loop, thereby affecting the concentrations of them that will be present, prior to amendment and the next re-injection pass through the loop.

Listed below are a just a few examples of possible conservative simplifying assumptions that might be used to identify the parameters for which ZOD permission is sought for a re-injection loop. The list is by no means exhaustive. If a conservative simplifying

assumption other than those listed below is proposed in a site-specific Remedial Action Plan, then it should be accompanied by an explanation, for the reviewer's acceptance on a case-by-case basis.

- If the site's contaminants of concern have only been partially treated prior to re-injection, and the identity of those that will be re-injected at concentrations in excess of their groundwater standards is not known with certainty, or may vary, then simplify matters by including all of the site's dissolved contaminants of concern in the list of parameters that may be in need of ZOD permission.

- If a chemical additive used for in situ aquifer remediation is added to a re-injection loop intermittently, or periodically as a batch-wise slug, then it may simplify matters to base the identification of parameters in need of ZOD permission on the chemical composition of the batch, just prior to the point of its introduction to the loop.

- If a chemical additive used for in situ aquifer remediation is continuously metered into a re-injection loop, and is expected to be completely consumed as it travels through the subsurface portion of the loop, then it may simplify matters to base the identification of parameters in need of ZOD permission on the chemical composition of the additive, just prior to its point of introduction to the loop.

- If a chemical additive used for in situ aquifer remediation is continuously metered into a re-injection loop, and is expected to be only partially consumed as it travels through the subsurface portion of the loop, then it may be necessary to conservatively estimate, for Remedial Action Plan preparation purposes, the amount of additive consumed in the subsurface portion of the loop. Since there is no actual data available, and a large number and types of chemical additives, and varying degrees at which they might be consumed, there is little that can be offered as advice. If consumption data does become available in the future for a particular additive, then use it to perform a dilution calculation for the mixing of recovered fluid with fresh additive prior to re-injection of the mixture, and base the identification of parameters in need of ZOD permission on the results of the calculation. Otherwise, in the absence of actual data, consider, for example, a consumption range of 10-50 percent for a low consumption additive, and 50-90 percent for a high consumption additive.

7. **Injection well permits and remediation plan approval orders.** Rule 62-528.630(2)(c), F.A.C., allows the authorization of injection-type aquifer remediation projects by way of Remedial Action Plan (RAP) Approval Order (or other enforceable Department approval mechanism) provided the construction, operation, monitoring, and injection well inventory requirements of Chapter 62-528, F.A.C., are met. This simply means that an enforceable RAP (or RAP Modification) Approval Order, or an Alternate Procedure Approval Order issued by the Department also serves as the state's permit for the construction and operation of a Class V injection well. As indicated in section 4 above, application of remediation products (or closed-loop recirculation of partially treated water) for the purpose of beneficial remediation of a contaminated site is allowed a ZOD

under the procedures described in this guidance whether the remediation products are applied to an injection well or another type of subsurface distribution system such as an infiltration gallery or application of a remediation product to the groundwater during a contaminated soil excavation. Only circumstances of using injection wells must be reported to the FDEP UIC Section, however, all circumstances of application of these products (or recirculation of partially treated water) must be authorized by issuance of an Approval Order by the Department.

8. **Professional Responsibility for RAP Recommendations and for Active Remediation.** It is not uncommon for the PE responsible for preparation of a RAP to consult with the vendor of a remediation product to determine the appropriate application rate and most effective method of delivery of the remediation product. However, the PE who signs and seals the RAP which is submitted to the Department must have a complete understanding of the proposed application of the remediation product to be able to verify that the proposed use of the product and the amount of the product to be applied is appropriate to meet the cleanup objectives of Chapter 62-770 and also that use of the product complies with applicable rules and procedures of the Department. Whether or not the company that prepares the RAP has a Performance Based Cleanup Contract with the vendor or with the Department has no bearing on this requirement.

   Additionally, it is not uncommon for the company that prepared the RAP to contract with the remediation product vendor or another subcontractor to perform the injection or application of the remediation product. However, the company which will submit the startup report, remedial action monitoring, and other reports and correspondence to the Department which asserts that the Department's rules and procedures have been complied with must have first-hand knowledge based on qualified staff being present during the injection events to document that the remediation product type, number of injection events, injection locations, quantity of product injected or applied, remediation product concentration, etc., is consistent with the approved RAP. Again, whether or not the company which will be submitting these reports to the Department has a performance based cleanup contract with a subcontractor or with the Department, or both, has no bearing on the need to comply with this requirement.

9. **Fate of injected chemicals**. It shall be incumbent on the manufacturer, vendor and user of an in situ chemical additive to ensure that a remediation chemical, upon release to the environment during an aquifer remediation project has no lasting harmful effects. Information about this topic may be included in a site-specific Remedial Action Plan or as part of a product evaluation request submitted to the Bureau of Petroleum Storage Systems' Innovative Technology Acceptance Program.

   a. **Residual Concentrations of Ingredients**. By the time that the cleanup of a site's contaminants of concern is complete, the residual concentrations of any ingredients of concern from the remediation chemicals used to clean up the site shall meet the applicable standards set for them in Chapters 62-550, 62-520, and

62-777, F.A.C., or their naturally occurring background levels at the site, whichever is less stringent.

b. **By-products**. By the time that the cleanup of a site's contaminants of concern is complete, the residual concentrations of any by-products produced, as a result of chemical or biochemical reactions induced by a remediation chemical used to clean up the site, shall meet the applicable standards set for them as maximum allowable drinking water contaminant levels in Chapter 62-550, F.A.C., general minimum groundwater criteria in Section 62-520.400, F.A.C., and chemical-specific cleanup criteria for groundwater (and soil) in Chapter 62-777, F.A.C. If a by-product chemical species is already present at a site prior to the start of a cleanup, and naturally occurring in concentrations that already exceed its applicable standard, then its residual concentration upon completion of the cleanup shall be no greater than its natural-occurring background level prior to the start.

Situations have arisen in which a site's contaminants of concern have been cleaned up to target levels, only to have the issuance of a Site Rehabilitation Completion Order delayed due to high residual concentrations of a remediation chemical's ingredients of concern in the zone of discharge. Person's responsible for contaminated sites undergoing site rehabilitation in accordance with Department cleanup rules and those environmental consultant firms implementing site rehabilitation actions on behalf of the responsible parties for the contaminated sites are hereby put on notice that they will be held responsible for meeting groundwater quality standards for the residual effects of ingredients of the remediation products which may remain after the target chemicals of site rehabilitation have been reduced to below groundwater standards. In order to minimize the occurrence of such situations, it is advised that the dosages and application rates of remediation chemicals be no greater than absolutely necessary to accomplish the objectives of a cleanup.

Possible remedies for such situations, in order of increasing cost, may include but are not necessarily limited to: (a) a zone of discharge time extension while the residual ingredients dissipate to acceptable concentrations; (b) groundwater recovery from areas of a site where the residual ingredient concentrations remain elevated, followed by proper offsite disposal; or (c) onsite treatment of the groundwater by appropriate methods for removal of the residual ingredients of concern. As of the publication date of this guidance, there is no data available in regard to the efficacy of any onsite treatment methods, since there have not been documented situations in which residual ingredient concentrations have been so highly elevated and/or persistent that treatment has been required. Method selection would obviously depend on the chemical species to be removed; for example: activated carbon for the removal of organics by adsorption; activated alumina for the removal of metals, halogens and sulfur; or ion exchangers for the

removal of cations and anions, provided the substitute ion itself does not exceed a groundwater standard.

10. **Foaming agents**. Foaming agents are regulated as secondary drinking water contaminants. The current maximum allowable concentration for them is 0.5 milligrams per liter. Foaming agents include surfactants, which may be of either the anionic, cationic, or nonionic type, although not all surfactants create foam. Method SM 5540 is a recognized laboratory method for the measurement of their concentration in water samples, and is published in *Standard Methods for the Examination of Water and Wastewater*. Method SM 5540 B, surfactant separation by sublation, isolates all surfactants, regardless of type. Method SM 5540 C is for anionic surfactants, and method SM 5540 D is for nonionics.

11. **Maintaining representative monitoring wells.** Chemical additives should not be applied directly to monitoring wells that are designated for the monitoring of a site's cleanup progress. However, if there are more monitoring wells than necessary for the tracking of cleanup progress, then some of the "extra" wells may be used for the injection of remediation chemicals. Once an extra well has been used for the injection of remediation chemicals, it is no longer available for use as a designated well for the monitoring of active remediation cleanup progress, but it still can be used for the monitoring of chemical species associated with a zone of discharge.

    The location of injection points for chemical additives, relative to the location of designated monitoring wells, should be such that the injection points are not so close as to skew the results of samples taken at the monitoring wells for a site's contaminants of concern. In other words: Do not install injection points too close to monitoring wells. If site-specific information about the effective radius of influence for the spacing of injection points is available, then this effective radial distance may also serve as the minimum distance to maintain between a monitoring well and the nearest injection point. In the absence of site-specific information, a rule of thumb would be ten (10) feet.

12. **Initiation of Natural Attenuation Monitoring or Post Active Remediation Monitoring following application of remediation products**. For some period of time after a remediation product is used, residual effects of the product on groundwater contaminant levels will continue, which will effectively depress groundwater sample analysis results for the chemicals which are the target of site rehabilitation. After there are no longer residual effects of the remediation product it is not uncommon for there to be a rebound in measured concentrations of chemicals which are the target of site rehabilitation in monitoring wells. For this reason it is not appropriate to begin Natural Attenuation Monitoring (NAM) or Post Active Remedial Action Monitoring (PARM) immediately following the application of the remediation products. The monitoring of chemicals which are the target of site rehabilitation which is conducted during this time before NAM or PARM may begin is considered to be Active Remedial Action Monitoring. The amount of time which must pass before the remediation product is no longer affecting the concentration of chemicals which are the target of site rehabilitation

in groundwater depends on the remediation product used and the application rate. The RAP which recommends the use of the remediation products must specify the basis to determine when active remediation monitoring is concluded and NAM or PARM may begin. This could be based on manufacturer's recommendations or the measurement of one or more indicator parameters in groundwater, such as dissolved oxygen.

If NAM or PARM had been initiated following a previous injection event, but due to persistent contaminant levels a decision is made to perform an additional injection of remediation products, then NAM or PARM must be discontinued and active remediation monitoring must once again be conducted after the subsequent injection event, and then NAM or PARM must start over once it is determined there are no longer residual effects of the remediation product on the results of analysis of groundwater samples.

13. **The use of chemicals for in situ soil remediation above the water table may, in some cases, require monitoring of the underlying groundwater**. Even in situations where a chemical is introduced above the water table, for the purpose of in situ soil remediation, it may still be necessary to monitor the underlying groundwater for its ingredients of toxicological concern. Such situations may arise when a soil remediation chemical is introduced at a depth that is close to the water table, or site conditions are such that its ingredients of toxicological concern could percolate or leach into the underlying groundwater even if the application depth is well-above the water table. In those situations, it is advisable to monitor the underlying groundwater for the remediation chemical's same ingredients of concern that would have been monitored for Underground Injection Control purposes, had the application been a direct injection into the groundwater. However, at this time these applications do not need to be reported by the cleanup programs to the Department's UIC Section. It may also be prudent to monitor the underlying groundwater for any of the site's contaminants of concern that could be carried downward to the water table by the remediation chemical.

14. **Open pit applications**. When used for beneficial cleanup of a contaminated site undergoing site rehabilitation under Department cleanup rules, application of remediation products to an excavation is considered to be a "subsurface fluid distribution system" and therefore may be authorized under the procedures of this guidance, including the need for prior authorization of the application of the product with an enforceable FDEP Order, establishing a zone of discharge, and post application monitoring of the residual effects of the remediation product. However, at this time these applications do not need to be reported by the cleanup programs to the Department's UIC Section.

15. **Bioaugmentation.** Non-indigenous microorganisms themselves are generally not classified as chemicals, but their use at a cleanup site, as in situ bioaugmentation should be given consideration with respect to Underground Injection Control requirements and groundwater criteria, in much the same way that consideration would be given to the use of an in situ remediation chemical. Natural-occurring microorganisms (not genetically engineered) are preferred, and they must be nonpathogenic (do not cause disease) in order to comply with the minimum groundwater criteria of Section 62-520.400, F.A.C.

16. **Innovative Technology Acceptance Process.** The Division of Waste Management has established a process for acceptance of innovative technologies and products used for contaminated site rehabilitation. The objective of this process is to foster a greater understanding of the various approaches to site rehabilitation that may be considered. As part of this process the Division of Waste Management issues innovative technology acceptance letters. These acceptance letters provide useful information on the regulatory requirements associated with use of the remediation products and processes. However, there are some limitations to the innovative technology acceptance process that need to be understood:

a. It is not necessary for an innovative technology acceptance letter to have been issued for a product or process for it to be proposed in Remedial Action Plan.

b. The term the Department uses for the letter of "acceptance" rather than "approval" has an important intent. A product or process with an innovative technology acceptance letter is subject to the same requirements for prior approval by the FDEP before being used for any particular application for site rehabilitation as a product or process which does not have an innovative technology acceptance letter. These products and processes may not be used for any specific site remediation activity without prior FDEP approval with an enforceable Order.

c. Though the innovative technology acceptance letters have useful regulatory information, the preparers of remedial action plans for responsible parties and the reviewers of remedial action plans for the Department should not rely solely on the content of the acceptance letter with its attachments for determining the design and monitoring requirements for remediation involving injection of remediation products. This guidance document along with applicable Department rules needs to be considered. Also, it should be understood that the innovative technology acceptance process has existed for more than ten years and some of the less recently published acceptance letters may not reflect the current regulatory requirements.

d. Some remediation products may have formulations which may have been disclosed to the Department as part of the innovative technology acceptance process but are treated as "trade secrets" under Florida Public Records law and thus, are exempt from general public disclosure laws and are kept in a separate location from the innovative technology file at the FDEP. In such case, if the formulation of the remediation product contains chemicals which might or might not exceed groundwater quality criteria at the point of injection, depending on the strength of the mixture, then the innovative technology acceptance letter may indicate a maximum strength of mixture that can be used without the need for post-injection monitoring of chemicals in the remediation product, or with monitoring of a limited number of chemical parameters. In this case the preparer of the Remedial Action Plan must adhere to this maximum strength of

formulation/dosage or otherwise be prepared to disclose the formulation to the FDEP or local program technical reviewer. To ensure that formulations that meet the statutory definition of a "trade secret" are not disclosed to the public, the law requires the preparer to clearly mark and identify the formulation as exempt from Florida Public Records law and the basis for claiming the formulation is a trade secret. The Department recommends that this information is contained either on the first page of the RAP or in the cover letter that is submitted with the RAP. See Sections 403.73 and 812.081, Florida Statutes. If it is necessary for the formulation to be disclosed to an individual technical reviewer for the FDEP, that technical reviewer will need to treat the submittal as exempt from public records and not scan to Oculus with the rest of the site correspondence.

More information on the innovative technology acceptance process including the list of products and processes with acceptance letters may be found at www.dep.state.fl.us/waste/categories/pcp/pages/innovative.htm

17. **UIC Reporting and other administrative considerations.** As indicated previously in this guidance document, with the exception of remediation products requiring a product specific variance as described in section 5 above, application of remediation products to groundwater or closed-loop recirculation of partially treated groundwater are automatically granted a ZOD provided the provisions of Chapter 62-520.310(8)(c), F.A.C., are satisfied, the procedures of this guidance are followed, and there is a RAP Approval Order or other FDEP order issued to authorize the remedial action. Remediation products which contain impurities that are not prime constituents of the remediation products are allowed a ZOD if a product specific variance is granted by the Department. For the cases in which the application of the remediation products or recirculation of partially treated water involves use of one or more injection wells (with a depth greater than the largest surface dimension of width or length), the proposed injection event must be reported to the FDEP UIC Section. The Division of Waste Management has created standard memorandum format for filing of these UIC Inventory reports. The UIC inventory report memo must be submitted to the UIC Section at the time of issuance of the Approval Order. This report memo must be completed by the Professional Engineer technical reviewer who completed review of the RAP or other engineering document on behalf of the Department. The person that prepared the RAP may complete portions of this template memorandum as a convenience to expedite review of the RAP by the Department and include the partially completed UIC notification memo as an attachment to the RAP. However, in this case the "FROM:" portion of the memo, the memo date, and the date of the Approval Order should be left blank. The PE responsible for the engineering document review for the Department will complete these portions after verifying the accuracy and regulatory correctness of the content of the memo.

Additional injection events not described in the approved RAP, or other engineering document which the Department approved with an Approval Order, are considered to be a RAP Modification and need to be separately authorized by the Department with another

Approval Order prior to implementation and must also be reported to the UIC Section. To avoid the need for subsequent approvals and UIC reporting, if the person preparing the RAP anticipates the possible need for additional injection events, these should be identified in the RAP or other engineering document as contingent injection events and may be reported to the UIC section as part of the proposed scope of remediation at the time of the Department's approval of the RAP. Notwithstanding this strategy of including contingency injection events in the remedial design to avoid the need for follow-up approval of a RAP Modification, any changes from the approved RAP as to details of the injection events, including the remediation product that will be used, an increase in the amount of remediation product to be injected per event, and the size or location of the zone of discharge, is considered a modification which necessitates prior Department approval and notification to the UIC Section.

An important consideration for FDEP funded cleanup sites is the accuracy of the cost estimate for alternative evaluation purposes to verify that the most cost-effective alternative has been selected. If the RAP for a funded site includes a recommendation for possible contingent injection events, the official recommendation of the preparer of the RAP for the number of injection events believed to be necessary to meet cleanup objectives, and which will be the basis for the cost-effectiveness evaluation of alternatives, and the cost associated with that proposed scope, needs to be clear. Once the RAP has been approved based on this recommended scope of injection, the Department will only issue a Work Order or Task Assignment for this scope of injection recommended in the RAP, regardless of whether or not the RAP also mentioned the possibility of future contingent injections. If the cleanup contractor wishes to modify the scope of injection after the RAP is approved, it may be necessary to first revisit the cost-effectiveness evaluation of the RAP.

18. **Disclosure of chemical additive ingredients.** For chemical additives that are injection-type aquifer remediation products, regardless of whether they are innovative or not, and regardless of whether they are proprietary formulations, a complete chemical analysis or description of the ingredients and their proportions in the fluid to be injected must be disclosed. Reason: In order for remediation plan approval orders issued by the Bureau of Petroleum Storage Systems to serve in lieu of operating permits for injection-type aquifer remediation wells, pursuant to Rule 62-528.640(1)(c), F.A.C., it must be ascertained that injected fluids meet the primary and secondary drinking water standards of Chapter 62-550, F.A.C., and the minimum groundwater criteria of Section 62-520.400, F.A.C. The Bureau also requests a disclosure of ingredients for non-injection type chemical additives as well, for toxicological reasons, in order to assure that no harmful substances are introduced to groundwater.

As indicated above in the innovative technology acceptance discussion, for formulations that are exempt from disclosure under Florida Public Records Law, the Bureau of Petroleum Storage Systems accepts the information on protected formulations and stores them in a location where access is limited. No exceptions will be made to the requirement of a complete disclosure, and no injection-type Remedial Action Plan or

innovative technology product proposal will be approved unless such disclosure is made. However, if an innovative technology acceptance letter has been issued by the Bureau of Petroleum Storage Systems, and the attachments to that letter indicate post injection monitoring requirements which are applicable provided that application rates are limited to a specific prescribed maximum dosage, then disclosure of the formulation to individual technical reviewers of the Department is not necessary provided those application rates are followed.

For the disclosure of ingredients in a chemical additive that are exempt from Florida's Public Records Law being proposed in a remediation plan or proposed in a submittal for an innovative technology product evaluation, a two-part submittal is suggested: the first part containing the nonproprietary public information, which may be voluminous; and the second part, stamped confidential, containing only one (1) copy of the page, or the few pages, which disclose the proprietary information.

19. **Migration to be avoided.** Pursuant to Rule 62-528.630(3), F.A.C., injection-type chemical additives for in situ aquifer remediation shall be injected in such a way, and at such a rate and volume, that no undesirable migration of either the product's ingredients or the contaminants which are the target of the site rehabilitation and are already in the aquifer results. A hydraulic analysis should be included in Remedial Action Plans as necessary to demonstrate this condition will be met.

For closed-loop re-injection type systems, in order to guard against the undesirable migration of contaminants, the hydrogeology of the specific remediation site should be taken into account during system design, to make sure there is adequate recapture of the re-injected fluids. In some cases it may not be a problem if fluids are withdrawn and re-injected into the aquifer at the same rate. In other cases, it may be necessary to create a contaminant-capturing effect by withdrawing liquid at a rate that is slightly greater than that at which it is re-injected. The excess fluid represented by the difference in these rates would of course have to be treated and/or properly disposed elsewhere, where it will not hydraulically interfere with the re-injection loop.

Installation of an adequate number of sentry wells just beyond the periphery of a closed-loop re-injection system, for regularly scheduled sampling, should be considered during system design. If during operation of the system these wells begin to detect unwanted contaminant migration, then it will be necessary to make an operating adjustment or to modify the system in order to stop the unwanted migration.

20. **Surface water considerations.** In cases where the site under remediation is in close proximity to a surface water body, including canals, the surface water criteria as well as the groundwater criteria need to be considered for both the chemicals of the remediation product and the target chemicals of remediation. Generally it is appropriate to identify one or more point of compliance monitoring wells near the boundary of the surface water body at which neither the surface water criteria nor groundwater criteria should be exceeded during site rehabilitation.

21. **Aquifer remediation chemicals for which no specific groundwater standards exist.** The absence of a specific primary or secondary groundwater standard, or minimum groundwater criterion for an aquifer remediation chemical should not be construed that the chemical is of no toxicological concern to humans or the environment. Additionally, toxicity concerns about aquifer remediation chemicals are not limited to only injection-type applications. The same toxicological concerns arise when chemicals are added to the aquifer by other means, such as spraying or spreading into an open excavation pit that has exposed the groundwater. If the chemical enters, or will enter the groundwater, then its toxicity should be considered.

Since it may be impractical and expensive to insist on development of a groundwater standard and a laboratory analytical method for every ingredient in every aquifer remediation product, the Bureau of Petroleum Storage Systems will, on a case-by-case basis, decide whether a groundwater standard should be developed. Once a standard is developed, however, the financial and technical onus shall be on the manufacturer and/or user to develop a method by which to measure the chemical's concentration in groundwater samples.

Chemicals such as food additives are generally considered benign to humans, but this does not necessarily mean that they are environmentally benign. Still, the chemical's use as a food additive, at the least, lends some support to making a case for its safety. Below is a list of sources that may be worth consulting when considering the toxicity of an aquifer remediation chemical for which a specific primary, secondary, or minimum groundwater standard does not exist.

- **EAFUS** (Everything Added to Food in the United States): An informational database maintained by the U.S. Food and Drug Administration (FDA) Center for Food Safety and Applied Nutrition.

- **ANSI/NSF Standard 60 certification**: The American National Standards Institute / National Sanitary Foundation. If an aquifer remediation chemical is certified in accordance with ANSI/NSF Standard 60, then the Bureau of Petroleum Storage Systems will recognize the certification. The Bureau will allow the use of the chemical for aquifer remediation, without groundwater monitoring of it, provided the dosage used does not exceed that which is recommended by the NSF for use as a drinking water treatment chemical. For dosages greater than those recommended by the NSF, the Bureau will require monitoring, and require the manufacturer or user to develop a laboratory analytical method for the analysis of the chemical in groundwater samples. Underwriter's Laboratories (UL) also performs Standard 60 certifications.

- **Algorithms in Chapter 62-777, F.A.C.** Chapter 62-777, F.A.C., provides equations by which groundwater cleanup target levels for chemicals can be calculated, provided

the proper toxicology data to be used in the equations is available in the literature. Use of the equations is not difficult; they are not complicated, but the Bureau, through its own experiences, has found that the required toxicology data to be used as input is seldom available for the chemical ingredients of aquifer remediation products.

If a *chronic oral reference dose* is known for a non-carcinogenic ingredient of a remediation chemical, then the value can be used in an equation to calculate a maximum allowable groundwater concentration for that ingredient. If the concentration of the ingredient in the fluid to be injected or introduced to the aquifer, for remediation purposes, does not exceed the calculated maximum allowable groundwater concentration, then the Bureau will not require that its concentration be monitored in the groundwater. For injection concentrations greater than the calculated maximum, however, the Bureau will require monitoring, and require the manufacturer or user to develop a laboratory analytical method for the analysis of the chemical in groundwater samples.

If the ingredient happens to be carcinogenic, then Chapter 62-777, F.A.C., provides an equation for the calculation of a maximum allowable groundwater concentration for such a substance. In order to use the equation, the value of an *oral slope factor* must be obtained from the literature.

22. **Safety.** Remediation plans and innovative technology proposals for chemical additives should include safety considerations. Depending on the nature of a chemical additive or remediation process involving chemicals, there may be many or relatively few safety considerations. Safety concerns include but are not limited to: toxicity; Material Safety Data Sheets; fire and explosion prevention; observance of the National Electrical Code; safe handling and storage of chemicals; safety devices; automated shutdowns of systems in the event of power failure or unsafe operating conditions; and personal protection of workers and minimization of exposure of them to hazards. Lists of safety topics can also be found throughout the Bureau's Remedial Action Plan Checklist and part 2 of the Innovative Technology Program application. In the case of remediation of petroleum contaminated sites which have active petroleum underground storage tanks (USTs), the RAP needs to specifically address safety plan considerations when using oxidants in close proximity to the USTs. Similar considerations should be given to use of oxidants at sites with occupied buildings when the proximity of the contaminated media and use of oxidants to the building could result in generation of vapors beneath the building.