February 26, 1999

EPA-SAB-EEC-COM-99-002

Honorable Carol M. Browner
Administrator
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, DC 20460

Subject: Waste Leachability: The Need for Review of Current Agency Procedures

Dear Ms. Browner:

The Science Advisory Board's Environmental Engineering Committee (EEC) has prepared this commentary to call your attention to the need to review and improve EPA's current waste leachability testing procedure, i.e., the Toxicity Characteristic Leaching Procedure (TCLP). This review involves two related issues. First, the TCLP is applied too broadly. Second, leach tests, including the TCLP when used to characterize toxicity, can be improved by accounting for additional parameters.

In 1990, EPA promulgated the TCLP as a method to characterize the toxicity potential of wastes using a particular worst-case scenario. In addition to its use as a waste classification test, the TCLP is being used by regulators and industry more broadly. The TCLP may be inappropriate in some of these broad applications.

The SAB raised many science issues to the Agency in its 1991 commentary, *Leachability Phenomena*. Many of these scientific issues remain current and, in some cases, affected Agency programs. For example, the Agency's reliance on a single scenario has caused some difficulties for the Agency's hazardous waste regulation programs. The Agency has had two significant legal challenges to the TCLP and its application in particular settings. An enclosure to the current letter also presents recommendations on leach test parameters and field issues. It is time to make improvements.

In the first case,[1] Edison Electric Institute challenged the application of TCLP for making hazardous waste classifications of mineral processing wastes, arguing that these wastes are never disposed in a municipal solid waste (MSW) landfill. While upholding the use of a generic mismanagement scenario, and noting that EPA is not obligated to tailor the TCLP to typical mismanagement conditions, the court concluded that the toxicity characteristic rule must bear "some rational relationship to mineral wastes in order for the Agency to justify the application of the toxicity test to those wastes."[2]

In a more recent instance, the use of the TCLP to determine compliance with a waste treatment standard was successfully challenged. In that case,[3] spent aluminum potliners were treated and disposed in a monofill which had conditions very different from those anticipated by the TCLP test. Landfill conditions such as high alkalinity, monofilling of waste, and very low ratios of leachate to waste (or liquid to solid) were important to waste leachability. Examination of the monofill leachate showed significantly higher concentrations of certain contaminants than those predicted by the TCLP test. When aluminum manufacturers challenged application of the TCLP in this setting, the court vacated this TCLP application. The court cited the language in the earlier EEI case, the Agency's failure to relate the TCLP test conditions to the actual field conditions, the significant difference in the field conditions, and the fact that waste contaminants were leaching at a much higher rate than predicted by the TCLP test.

These cases support the view that EPA needs greater flexibility in waste leach testing, and that EPA's leach testing needs to account for more leaching parameters because they affect actual leaching of contaminants from waste in the field.

The current state of the science supports, even encourages, the development and use of different leach tests for different applications. To be most scientifically supportable, a leaching protocol should be both accurate and reasonably related to conditions governing leachability under actual waste disposal conditions.

The science supports consideration of scenarios other than the municipal solid waste scenario on which the TCLP currently relies for determining the whether wastes meet the toxicity characteristic. When leach testing is applied in a regulatory program to characterize toxicity, it may be appropriate for the leaching protocol to be waste-specific within the context of one or more accepted generic worst-case mismanagement scenarios. The same scenario(s) may not be appropriate for other applications, such as site remediation or waste treatment evaluation. For some applications it may be better to use the worst case scenario likely to be encountered in the field. When a leachability test is used to assist with an environmental assessment of a particular location, it may be more appropriate for the test to be both waste and site specific. While this approach may require more case-specific analysis, it should yield more reasonable results.

**The Committee's single most important recommendation is that EPA improve leach test procedures, validate them in the field, and then implement them.** The Agency recognized this need in 1990 when it stated, in the TCLP final rule, that "the present TC revisions are only the first step in a long-term strategy to refine and expand the hazardous waste identification program." The EEC's 1991 commentary, *Leachability Phenomena*, recommended improvements to leach test procedures. EPA has not used these recommendations to revise the TCLP or to develop other Agency sanctioned leaching protocols.

The Committee recognizes the difficulty of developing different leach tests for different applications while at the same time retaining sufficient consistency and commonality to be both workable and logical. Maximum use should be made of a conceptual model followed by an analogue model with good statistical rigor. Nevertheless, the Committee recommends that the Agency study the TCLP testing procedure -- and its various applications -- and then generate improved leach test procedures. The Committee is confident that leach test procedures can be improved within the constraints of the regulatory environment and the operational needs of available laboratory procedures.

The multiple uses of TCLP may require the development of multiple leaching tests. The result may be a more flexible, case-specific, tiered testing scheme or a suite of related tests incorporating the most important parameters affecting leaching. Applying the improved procedure(s) to the worst-case scenario likely to be encountered in the field could ameliorate many problems associated with current procedures. Although the Committee recognizes that these modifications may be more cumbersome to implement, this type of protocol would better predict leachability.

Many parameters that affect the leachability of contaminants in the field are not addressed in the current TCLP. Indeed, it would be difficult to accommodate all the parameters affecting leaching into a single protocol. However, the most important of these parameters should be considered. Although the Committee does not offer any advise to the Agency, at this time, on which parameters will be most important to consider for the various applications, the Enclosure discusses many of these parameters and their effects. Because this is a large undertaking, the EEC suggests that EPA first upgrade the primary uses of the TCLP and then address ancillary uses of the test.

The EEC would be happy to assist the Agency in providing consultation on specific issues germane to the revision of the Agency's leaching protocols. We look forward to the response of the Assistant Administrator for the Office of Solid Waste and Emergency Response.

Sincerely,

/signed/
Dr. Joan Daisey, Chair
Science Advisory Board

/signed/
Dr. Dr. Hilary Inyang, Chair
Environmental Engineering Committee
Science Advisory Board

/signed/
Dr. Domenico Grasso, Chair
Leachability Subcommittee
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# ENCLOSURE A

1) **Background**: The Resource Conservation and Recovery Act (RCRA) defines hazardous wastes as solid wastes that may pose a substantial present or potential hazard to human health and the environment when improperly managed. The Agency promulgated characteristics that classify wastes as hazardous by virtue of their inherent properties (45 FR 33084). In this final rule, the Agency established two criteria for identifying hazardous waste characteristics: "1) The characteristic should be capable of being defined in terms of physical, chemical or other properties which cause the waste to meet the statutory definition of hazardous waste and 2) the properties defining the characteristic must be measurably standardized and available testing protocols." Under this rule, the potential for certain wastes to leach significant concentrations of toxic substances is a defining characteristic. In order to identify wastes which may exhibit such leaching behavior, the Agency, at present, uses the TCLP.

The TCLP results from EPA's efforts to improve upon the earlier Extraction Procedure (EP) Toxicity Characteristic (EPTC). The major shortcomings of the EPTC were its inaccuracy when applied to organic constituents and the lack of useful benchmarks for determining toxicity levels. The Hazardous and Solid Waste Amendments (HSWA) in 1984 directed EPA to make changes in the testing procedure to predict the leaching potential of a waste more accurately. To better address the leaching behavior of organic compounds, EPA replaced the EPTC with TCLP. The TCLP, like EPTC, assumes a worst case mismanagement scenario involving co-disposal in a MSW landfill.

Two difficulties with the TCLP are: a) the TCLP does not account for the many parameters that affect leaching; and b) the TCLP has been applied in situations where it is not appropriate. The latter is important because a test designed to predict leaching in MSW landfills may over- or under-predict leaching potential in other scenarios. Given the broad-based application of TCLP, scientific issues related to its appropriateness as a predictor of leaching must be addressed in the general context of its use. Section 4. addresses leach test parameters in some detail.

This commentary focuses on issues associated with the TCLP regarding the breadth of its application and the need to account for a wider range of parameters. The 1991 EEC commentary, *Leachability Phenomena* (EPA-SAB-EEC-92-003), identified concepts and principles that should be incorporated into any analytical protocol that is aimed at assessing contaminant leaching potential from wastes.

More specifically, *Leachability Phenomena* recommended an Agency-wide effort to:

a) study and better understand mechanisms controlling leachability,

b) develop better conceptual models for waste management scenarios

c) evaluate stresses affecting long-term contaminant release potential

d) develop a variety of contaminant release tests and test conditions to assess potential release of contaminants from sources of concern

e) improve mathematical models to complement laboratory tests of leachability

f) field test leach tests before being broadly applied

Ideally, testing procedures bear a rational relationship to the actual conditions under which waste is managed and consider the many parameters that affect the leaching behavior of contaminants from a waste. The TCLP does not address all parameters and scenarios. As a result, the TCLP is more accurate in some applications than in others.

Where important parameters are not considered and the scenario does not relate to actual disposal conditions, decisions based on the test results may not protect the environment or human health. *Leachability Phenomena* pointed out that "prior to developing or applying any leaching tests or models, the controlling mechanisms must be defined" and "an understanding of how they (directly or indirectly) influence release and environmental fate should be established."[4] *Leachability Phenomena* stated that "any extrapolation of a set of conditions or stresses appropriate for one purpose should not be applied to another without reasonable verification of relevance."[5] Moreover, such extrapolation must be scientifically and legally defensible.

The remainder of this enclosure describes the TCLP test and its recent uses, discusses leach test variables in light of both waste classification and risk assessment, and presents issues pertinent to waste management in the field that should impact the development and implementation of an appropriate test. Finally, any EPA leaching test must insure statistically rigorous methods for sample acquisition and analyses that minimize uncertainty and maximize the likelihood of accurate and representative results.

2) **Description of the Toxic Characteristics Leaching Procedure**: The Toxicity Characteristics Leaching Procedure (TCLP) is a batch test developed by the EPA in response to deficiencies in the Extraction Procedure (EP).[6] Many of the assumptions used in developing the EP were retained. For example, the TCLP models co-disposal of industrial waste with municipal solid waste in a sanitary landfill. The model assumed 5 percent industrial solid waste and 95 percent municipal waste.[7] However, the TCLP has important differences from the EP.

The TCLP specifies a procedure for liquid wastes, which are those with less than 0.5 percent dry solid material and for wastes containing greater than or equal to 0.5 percent dry solid waste. For liquid wastes, the waste is filtered through 0.6-0.8 $\mu$m glass fiber filter. The liquid after filtration is defined as the TCLP extract. For wastes containing greater than or equal to 0.5

percent dry solid waste, the liquid must first be separated and stored for later analysis. The solid phase may then undergo size reduction.[8] The EP required particle size reduction where the waste could not pass through a 9.5-mm sieve or has a surface area of less than 3.1 $cm^2$/gm. This requirement is retained by the TCLP. However, where the EP allowed the use of the Structural Integrity Procedure (SIP) for monolithic wastes, the TCLP does not. The SIP accounts for the effects of waste material physical durability on contaminant leachability. In the TCLP, the waste must be ground or milled until it passes a 9.5-mm sieve.

While the EP used only one extraction fluid, the TCLP uses two. A pH 2.9 acetic acid solution is used for moderately to highly alkaline wastes and a pH 4.9 acetate buffer solution is used for all other wastes.[9] The TCLP also uses two types of extraction vessels. For volatile compounds, a zero headspace vessel is used while bottles are used for non-volatile compounds.[10] The TCLP specifies rotary agitation in an end over end fashion at 30±2 rpm. The extraction period for the TCLP is set at 18 hours.[11] The extraction fluid is filtered using a 0.6-0.8 $\mu$m glass fiber filter.[12] Unless multiple phases will form on combination, the extraction fluid is combined with the initial liquid phase. The combination is then analyzed. Otherwise, the liquids are analyzed separately and then mathematically combined to give a volume-weighted average concentration.[13]

3) **Uses of TCLP**: Although promulgated as a test of the toxicity characteristic of contaminants in a waste, TCLP has found a variety of other applications. For example, TCLP has been used in administrative delisting procedures, as an end point test for clean-up standards and as a source term (often implying an infinite source) for risk assessments/site closure modeling.

The appropriateness of employing TCLP for these and other uses is questionable because the TCLP does not account for the variety of processes which can affect leachate quality, quantity and migration. Not all of these factors are equally important in every situation, of course, which makes guidance particularly important. The Committee recommends that the EPA consider issuing a policy statement on the appropriate use -- and limitations -- of the TCLP and/or other leaching tests. EPA should also consider developing guidance on the relative importance of each parameter as it pertains to particular applications (such as waste delisting petitions, source term estimates, etc.)

4) **Leach Test Parameters**

a) **Kinetics**: The TCLP is based on an extraction time of 18 hours. This time frame was arbitrarily chosen and does not necessarily bear any relation to an equilibrium state. Moreover, the point at which the system is poised in relation to equilibrium will be variable. For some constituents, the 18-hour extraction period could approximate the time to equilibrium. However, for others, it could be years away. Moreover, mass transport domains governing batch leaching in the TCLP are physically quite different from flow regimes experienced in the field. Some solid matrices display a long period of slow release that may be more relevant to the protection of health and the environment than the early, fast release. This slow release may or may not persist above the regulatory levels. For some constituents, the TCLP may not measure this slow release. Consequently, the extensibility of TCLP data to developing an understanding of the mobility of contaminants in the field is tenuous. However, as the *Leachability Phenomena* document pointed out, in the majority of contaminant release cases, the equilibrium situation does not apply with the result that rate limiting chemical and physical reactions are more important to the analysis.[14]

Therefore, quantifying the kinetics of release is of significant importance. Determining the controlling mechanisms for the scenario and selecting appropriate testing periods should improve the accuracy of the leach test(s).

b) **Liquid/Solid Ratio**: The TCLP uses a 20:1 liquid to solid ratio. This ratio was chosen for analytical and administrative procedural purposes. In the field (in either MSW landfills or natural environments), liquid to solid ratios can vary significantly depending upon conditions. Variables such as weather, climate and infiltration rates as well as hydrological impacts of engineered systems can result in substantial deviations from this ratio. Furthermore, if saturation is experienced, the relative solubility of some constituents may be suppressed.

It is especially important to consider such variables where the leach test is being used to predict behavior in the field.

c) **pH**: The TCLP assumes that, in the MSW landfill scenario, the disposal venue (not the waste) governs the leaching fluid chemistry. The two current TCLP leaching fluids cannot account for the full diversity of wastes and waste management conditions. As a result the TCLP does not always accurately predict the concentrations of various constituents that will actually be found in leachate. For example, a recent study indicated that pH values of MSW leachates (pH 6-8.5) were generally higher than pH values used in the TCLP.[15] This difference in pH was thought to cause the higher than predicted concentrations of regulated metals that form oxoanions (e.g., Sb, As, Mo, Se, V) in MSW leachate. Many contaminants do not leach from waste matrices.

The treatment of alkaline wastes is another difficulty because the TCLP may underestimate the leaching potential of such wastes. First, continuous long-term contact with an acidic medium may exhaust the alkalinity thus increasing the leaching potential of an alkaline waste. Second, the leachability of certain waste constituents may increase under alkaline conditions.

Similarly, aggressive simulated MSW leachate (i.e., TCLP fluids) may significantly over predict the availability and mobility of contaminants in natural settings. It is doubtful that any test will address the full diversity of conditions at sites at which wastes are managed. Modeling is another way to address this difficulty.

Addressing such situations, in which field chemical conditions are not well represented by the TCLP[16] , should result in improvements to the leach test procedure(s).

d) **Colloid Formation**: Colloids may be formed during the end-over-end agitation required in TCLP testing. The forces exerted during the agitation process may overcome the adhesion or cohesional forces of some constituent particles. This aggressive agitation can dislodge or otherwise create colloidal particles, which may pass through the filtering process and subsequently be analyzed as part of the extract. Hydrophobic organics and metals can preferentially bind to these colloidal particles. The detached colloidal particles in the extraction fluid may result in an over-prediction of the aqueous phase of the constituent by the TCLP. [17]

Colloidal phase constituents may not be representative of field speciation and should be treated differently from dissolved constituents in risk analyses. An appropriate and representative solid/liquid separation procedure should be incorporated into the revised testing procedures.

e) **Particle Size Reduction**: TCLP particle size reduction requirements may not represent field conditions. The TCLP requires that solids must be reduced in size to pass a 9.5-mm sieve before the waste is mixed with the extraction fluid. This reduction in size increases the specific surface area of the particles, which increases the leaching potential. Monolithic wastes have a lower leaching potential due to physical stabilization and the resultant increase in the length of the diffusion pathway from waste into the leachate. Additionally, some processes also provide for chemical stabilization by binding heavy metals in insoluble hydroxide and other complexes.[18] Consequently, reductions in leachability that derive from solidification/stabilization associated with monolithic wastes are ignored.[19]

*Leachability Phenomena* recommended that low strength wastes should be milled. Moderate strength wastes should be tested sequentially as they are gradually reduced in particle size. High strength wastes could be agitated “as is.” Further, the commentary asserted that wastes agitated “as is” will break up leaving only stronger portions intact.[20] This “as is” agitation may more accurately represent the conditions in which the waste exists.

Reduction in particle size also affects testing of volatile compounds. Although the use of the zero headspace extractor vessel (ZHE) reduces the loss of volatiles during sample preparation procedures, particle size reduction of a waste containing volatiles will result in losses before the waste is introduced into the ZHE. The problems with particle size reduction were discussed in the proposed rule in which the TCLP was introduced. EPA concluded that the advantages of particle size reduction outweighed the potential problems. In light of the comments above, the Committee recommends that EPA revisit the issues of volatile loss and/or increases in constituent solubility.

f) **Aging**: At present, the TCLP protocol requires that wastes be tested at the time of generation. Should significant time elapse from time of generation to time of disposal, chemical or physical transformations may take place compromising the validity of TCLP results as a predictor of leachable concentrations.

Similarly, if a leach test is used for risk assessment purposes, it should accommodate transformations that may be expected over the time frame of model predictions. The Agency should address aging considerations in its revised protocol.

g) **Volatile Losses**: The volatility of the waste may result in losses during the leaching procedure and analysis. The EPA requires the use of a zero-headspace extraction vessel (ZHE) when testing volatiles. However, as discussed above, sample handling (e.g., particle size reduction) may also result in loss of volatile compounds. Additionally, when addressing volatile compounds, the most important pathway for release to the environment may not be leachability. The mass release through volatile losses must be considered in these cases.

h) **Interaction with Other Wastes**: The TCLP assumes municipal solid waste leachate governs leachate chemistry and rate of release. However, many other scenarios are possible, some of which may lead to an increase in the leachability when compared to the standard generic case.

*Leachability Phenomena* pointed out that, in the presence of co-solvents, solubility of the constituents in the organic phase rather than aqueous phase may control the leachate concentration.[21] Similarly, surfactants may also mobilize hydrophobic contaminants. Testing procedures and analyses of results should address the issues associated with the presence of co-solutes in either a waste classification or risk assessment scenario.

5) **Related Field Issues**

a) **Multiple Phases**: At some contaminated sites, residually trapped mixtures of hydrocarbons exist which take the form of non-aqueous phase liquids (NAPL). The release of chemicals into groundwater is affected by both the dissolution of the

NAPL mixture and desorption from the soil matrix.[22] The multi component release from the residually trapped mixture must be considered to accurately predict contaminant concentrations. When testing a multi-component NAPL mixture with the TCLP, the more soluble fraction will dissolve first, yielding an inaccurate portrayal of the behavior over a longer period of time. Similarly, precipitation and dissolution reactions may bias TCLP results away from what may be observed in the field. Procedures to accommodate the potential presence of multiple phases should be developed.

b) **Field Validation of the Test**: The 1991 EEC commentary, *Leachability Phenomena*, suggested that leach tests should be field validated before broad application. By simulating field conditions with appropriate test variables, more accurate and precise results can be achieved.[23] The TCLP was not intended to be representative of in-situ field conditions but rather of a generic MSW landfill worst case scenario. There should be a means for reconciling any leach test results with expected or observed field leachate concentrations. The use of an appropriate model would be helpful in this regard. Modeling and/or monitoring could help in defining such field conditions, and then provide a framework for possible use of the TCLP results within a site-specific risk assessment framework Consequently, should the ultimate disposal scenario for either risk classification or risk assessment be significantly different than the MSW landfill case, field validation of any revised protocol may be necessary.

Wastes sampled from different locations at the same site could yield different results. The contaminants themselves could also be different from one area of a site to another. This heterogeneity could affect concentrations in the leachate and interactions between co-disposed wastes. For either the waste classification case or the risk assessment case, a rigorous statistically based sampling protocol to account for representativeness and to minimize uncertainty should be developed and adopted.

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## ENDNOTES

[1] *Edison Electric Institute v. U.S. Environmental Protection Agency*, 2 F.3d 438, 443 (1993).

[2] Id. at 446.

[3] *Columbia Falls Aluminum Co. v. U.S. Environmental Protection Agency*, 1998 WL 151176 (D.C. Cir.).

[4] Id. at 8.

[5] Leachability Phenomena, EPA-SAB-EEC-92-003, p. 13 (October 1991).

[6] Identification and Listing of Hazardous Waste, 51 Fed. Reg. 21,653 (1986).

[7] Id.

[8] Identification and Listing of Hazardous Waste, 55 Fed. Reg. 11,863 (1990).

[9] Identification and Listing of Hazardous Waste, 51 Fed. Reg. 21,678 (1986).

[10] Id.

[11] Id.

[12] Id.

[13] Identification and Listing of Hazardous Waste, 55 Fed. Reg. 11,865 (1990).

[14] Id. at 10.

[15] Hooper *et al.*, "Toxicity Characteristic Leaching Procedure Fails to Extract Oxoanion-Forming Elements that are Extracted by Municipal Solid Waste Leachates", *Environmental Science & Technology*, 32, 3825-3830 (1998).

[16] Identification and Listing of Hazardous Wastes, 51 Fed. Reg. 21655 (1986).

[17] J. Bergendahl, D. Grasso. "Colloid Generation During Batch Leaching Tests: Mechanics of Disaggregation", *Colloids and Surfaces, A: Physiochemical and Engineering Aspects*, 135, 193-205 (1998).

[18] Identification and Listing of Hazardous Wastes, 51 Fed. Reg. 21656-57 (1986).

[19] Identification and Listing of Hazardous Waste, 51 Fed. Reg. 21,656-57 (1986).

[20] Leachability Phenomena, EPA-SAB-EEC-92-003, p. 12 (October 1991).

[21] Id. at 7.

[22] W.G. Rixey, Sanjay Garg, Pravin Murkute, Wei Qu. "The Effect of Aqueous Aging on the Fixed Bed Desorption of Benzene, Toluene, m-Xylene, and Naphthalene from Soil", Submitted , *Journal of Bioremediation* (1998).

[23] Leachability Phenomena, EPA-SAB-EEC-92-003, p. 14 (October 1991).