

Risk Evaluation of Leachable Mercury From Concrete Products Made With Fly Ash

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ABSTRACT

AES Hawaii, Inc. operates a 203 Megawatt circulating fluidized bed coal and alternative fuel-fired cogeneration facility. A portion of the byproduct fly ash may be used as a concrete admixture. Per AES Hawaii's solid waste management permit (SWMP), composite samples of fly ash are routinely tested for total and leachable metals content. In 2005, several samples exceeded the permit limit for leachable mercury (0.00025 mg/L) determined through the Synthetic Precipitation Leaching Procedure. AES Hawaii prepared a risk evaluation to determine if mercury from fly ash posed an environmental concern when intermixed in concrete products.

The primary objectives of the risk evaluation were to: 1) evaluate whether incorporating fly ash into concrete/flowable fill reduces mercury leachability to acceptable levels; and 2) determine if a threshold fly ash content exists that results in unacceptable mercury concentrations in concrete/flowable fill leachates. The study demonstrated that, even in cases where mercury in the raw fly ash exceeds the SWMP limit, no detectable mercury is leachable from the final concrete products containing such fly ash. In addition, since no mercury was detected in leachates, no threshold of fly ash content (up to 90 percent cement replacement) appears to exist where leachable mercury exceeds the applicable risk-based limits. As such, mercury in AES Hawaii fly ash used as an admixture in concrete products does not pose an unacceptable risk to human health or the environment. The Hawaii Department of Health therefore proposed an increased mercury limit for such fly ash from 0.00025 mg/L to 0.0055 mg/L.

INTRODUCTION

AES Hawaii, Inc. (hereafter AES Hawaii) operates a 180 Megawatt net circulating fluidized bed coal and alternative fuel-fired cogeneration facility, the only such facility on the Island of Oahu and the only operational coal fired plant in operation in Hawaii. This operation generates approximately 15 to 20 percent of Oahu's electricity. Coal combustion ash is a by-product of AES Hawaii operations from burning coal and alternative fuels for electricity generation. Fly ash and bed ash are mixed to form

conditioned ash, some of which was reused in concrete and the surplus was deposited in a private quarry for land reclamation. The quarry had reached capacity and would no longer accept the fly ash, requiring future disposal at a permitted landfill. In an island environment which by design has land limitations, the option of continuing to use a portion of the fly ash as an admixture by Hawaiian Cement in its concrete products was considered highly desirable.

Under AES Hawaii's solid waste management permit (SWMP) issued by the Hawaii Department of Health (HDOH), the fly ash is routinely tested via the SPLP for suitability for use in concrete by measuring the total and leachable metals content of composite samples. The SPLP analysis is designed to measure how likely the chemicals present in a solid material are to be released into surface water or groundwater when exposed to precipitation. In 2005, several composite fly ash samples submitted for routine analysis exceeded the permit limitation for leachable mercury (0.00025 mg/L) (refer to Figure 1). AES Hawaii retained URS Corporation (URS) to conduct a risk evaluation to determine if mercury from fly ash posed an environmental concern when intermixed in concrete products.

The major components of the risk evaluation were to identify potential risks, design a quantitative study to evaluate the potential risks, analyze the results of the study, and propose alternate permit conditions dependant upon those results.

IDENTIFICATION OF POTENTIAL RISKS FOR EVALUATION

Two potential risk issues were identified for mercury in AES fly ash subsequent to its inclusion in concrete products: 1) direct contact with mercury release during mixing or from weathered concrete, and 2) leaching of mercury from the concrete to surface water or groundwater. Further evaluation eliminated the first potential risk as unlikely based on the following rationale:

- During combustion, mercury in coal volatilizes and is emitted in the flue gas. Some of the mercury contained in the flue gas (predominantly ionic mercuric compounds such as HgCl_2 and HgSO_4) then adsorbs to the carbon phase of the coal ash as it cools. The presence of volatile elemental mercury in the fly ash is unlikely. As such, volatilization is not considered an important fate and transport mechanism in the fly ash product.
- Because total concentrations of mercury in the fly ash (typically 0.2 to 0.4 milligrams per kilogram [mg/kg]) are well below Hawaii's risk-based screening criterion for mercury of 13 mg/kg at contaminated sites (HDOH, 2005), as well as the United States Environmental Protection Agency (USEPA) Region IX residential preliminary remediation goal (PRG) (USEPA, 2004a) of 23 mg/kg (for "mercury and compounds"), direct contact with fly ash (dermal, oral, or inhalation of particulates) by residents or workers is also not considered a potential health issue.

The second potential risk remained for further evaluation because the inorganic mercury compounds bound to fly ash particles could have the potential to be released into an aqueous phase when exposed to water in the environment. Therefore, the risk evaluation was designed to address potential concerns if mercury bound into concrete were to be found leachable into surface water and groundwater.

RISK EVALUATION PURPOSE AND OBJECTIVES

The primary objectives of the risk evaluation were two-fold: 1) to evaluate whether mixing fly ash with cementitious material to form concrete or flowable fill reduces the leachability of mercury to acceptable levels; and 2) to determine if a threshold of fly ash content exists that results in unacceptable mercury concentrations in the SPLP leachate of the concrete. Secondary objectives included investigating whether a difference exists in mercury leachability between intact and crushed (recycled/weathered) concrete, and whether an extraction fluid simulating the pH of rainwater on the leeward coast of Oahu influences mercury leachability. These secondary objectives were designed to be studied in the event that mercury was detected in the SPLP leachate upon mixing with concrete. With HDOH approval, these secondary objectives would be dropped from the evaluation if the SPLP leachate, under “worst case” conditions, did not contain mercury.

STUDY DESIGN

The study would be conducted in two stages, each stage designed to assess the primary and secondary objectives, respectively. The first stage would compare “worst case” analytical results from SPLP testing of concrete cylinders containing varying percentages of ash with varying concentrations of mercury against applicable risk-based criteria. If detectable mercury levels were to be identified during the first stage, the second stage of the study would then result in collection and comparison of analytical results from SPLP testing procedures modified to represent “real world” environmental affects on the same concrete cylinders.

Hawaiian cement concrete products are used throughout Hawaii in a variety of land and marine applications, thereby prompting a multi-pathway evaluation. Based on these potential exposure pathways, applicable criteria for comparison with SPLP results were identified in advance of analytical testing. These criteria, in conjunction with the established permit limit, were used to set the appropriate method detection limits for SPLP testing in an effort to minimize study uncertainties.

TECHNICAL APPROACH

The technical approach involved reviewing analytical data from 2005 to select archived samples appropriate to the study’s objectives, re-analyzing the 2005 results and raw materials from Hawaiian Cement to establish a study baseline, and preparing and curing concrete cylinders according to industry standards with varying levels of ash replacement to represent permitted mixtures and flowable fill. The first stage of the

study then concluded with the analysis of the cured cylinders per Total Mercury and SPLP method requirements.

Sample Selection and Study Baseline

AES Hawaii's routine monitoring program includes semi-monthly compositing of fly ash samples for analysis. One grab sample is taken of each ash type for each day of shipment. Each composite consists of portions of these discrete grab samples taken during the designated time period, combined by laboratory personnel and analyzed for total and leachable metals. A portion of each grab sample is archived at AES Hawaii.

Using the monitoring data from 2005, eight semi-monthly composites were identified that yielded leachable mercury concentrations above the method detection limit (MDL) at varying ranges appropriate to the study's objectives (refer to Figure 1). URS' laboratory, Geotesting Services, Inc., combined the archived grab samples associated with those time periods as appropriate to recreate the original composite samples. The new composites were then submitted to a subcontracted laboratory for analysis to confirm the original fly ash SPLP mercury results prior to testing concrete made from varying percentages of those composites. Small quantities of Portland cement, #4 basalt, and sand obtained from Hawaiian Cement were submitted for analysis as well, to verify that these constituents would not contribute mercury to the final product.

A summary of the original monitoring data and the new data is presented in Figure 2. The SPLP mercury results generated by the study baseline testing were somewhat different than the original results. Specifically, where previously six of eight samples exceeded the permit limit of 0.00025 mg/L, in the new data set, only one sample exceeded that level. Although the concentrations differed somewhat, the new analyses confirmed within acceptable precision that there was a trace amount of leachable mercury present in most of the samples tested, which, in at least one case, exceeded AES Hawaii's permit limit for fly ash. Based on the old and new data, the four samples with the highest leachable mercury content and greatest amount of remaining sample material were selected to conduct the risk evaluation testing (refer to Figure 2)

Cylinder Preparation and Curing

From the three selected composites, Geotesting Services prepared batches of concrete using the ratio of materials contained in Hawaiian Cement's concrete, replacing 25 percent and 50 percent of the Portland cement with each fly ash composite. In addition, batches of flowable fill were prepared by replacing 90 percent of the cement with each of the three fly ash composites. The proportions of materials in each of these mixes (based on batch weights provided by Hawaiian Cement) are summarized as follows in Table 1.

**Table 1.
Summary of Concrete Mixtures for Analysis
By Percent Cement Replacement with Fly Ash**

Materials	Percent of Material by Weight		
	Concrete		Flowable Fill
	25% Fly ash*	50% Fly ash*	90% Fly ash*
No.4 Basalt	60.9	60.9	61.3
Sand	15.3	15.3	0.0
Water	8.3	8.3	15.0
Cement	11.6	7.7	2.4
Fly Ash	3.9	7.7	21.4

* Percent of cement replaced with fly ash.

One batch of concrete was prepared containing no fly ash to serve as a control. The concrete and flowable fill mixtures were placed in 2-inch-diameter cylindrical molds and moist-cured for 28 days (for consistency with industry standards) prior to chemical analysis. At least three cylinders were prepared for each mixture, plus an additional three cylinders for one 50 percent mixture, to allow duplicate analyses for quality control (refer to Figure 3). To simulate weathered conditions, a portion of the cylinders were crushed. The crushed cylinders were considered a worst case condition because the smaller components would have a larger surface area, thereby enhancing the potential for leaching of mercury.

ANALYTICAL RESULTS

The analytical data for total mercury in the crushed concrete samples are summarized in Figure 4. The total mercury concentrations ranged from less than 0.007 mg/kg to 0.037 mg/kg, well below the 13 mg/kg permit limit. No mercury was detected in the SPLP leachates of any of the crushed concrete samples, relative to a reporting limit of 0.0001 mg/L and a method detection limit of 0.00002 mg/L. As such, it was considered unnecessary to proceed with the previously described Stage 2 of the study. Since the SPLP results were all non-detect, the leachable portion of the total mercury content was, for the purposes of this study, effectively zero.

RISK EVALUATION

AES Hawaii's permit criterion for leachable mercury was promulgated on the State of Hawaii Tier I Environmental Action Level (EAL) for water (HDOH, 2005). In general, Tier I action levels are conservative criteria set to be protective of human health and aquatic life under most exposure scenarios. However, since AES Hawaii fly ash is not reused as a stand-alone product, but rather as a component of a Hawaiian Cement concrete product, and SPLP mercury levels from concrete made with fly ash were all non-detect, AES Hawaii requested the risk evaluation include a proposed alternative permit limit that would be applicable to fly ash used as a concrete additive.

Pathway Determination

Since Hawaiian Cement concrete products are used in various settings throughout the island of Oahu (and possibly elsewhere in Hawaii), the risk evaluation considered the most sensitive receptors for each pathway determined to be complete in the conceptual site model. Figure 6 provides a pictorial conceptual site model (CSM) of how leachable constituents in selected concrete products could be released and reach human and ecological receptors. These receptors were (a) a human drinking water user, (b) a recreational fisherperson, (c) various freshwater aquatic organisms, and (d) various marine aquatic organisms.

Comparison of SPLP Mercury Results with Applicable Criteria

In addition to the permit limit for mercury of 0.00025 mg/L, which is based on the most stringent water standard (i.e., the protection of marine aquatic species and habitat under chronic conditions) with an attenuation factor of 10 applied, the SPLP mercury results were compared to other commonly used risk-based criteria for the identified receptors of concern as discussed below. These criteria include:

- Environmental Action Levels presented in “Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater,” (HDOH, 2005);
- The State of Hawaii water quality criteria listed in the Hawaii Administrative Rules, HAR §11-54-4(b)(3);
- The ambient water quality criteria (AWQC) included in “National Recommended Water Quality Criteria: 2004” (USEPA, 2004b); and
- The National Primary Drinking Water Regulations (USEPA, 2002).

Figure 6 presents a summary of the potentially applicable criteria by receptor type and pathway, compared to SPLP mercury results.

Basis for Permit Limit

The existing mercury permit limit (0.00025 mg/L) is derived from the HDOH marine chronic aquatic habitat goal (based on the Hawaii chronic saltwater surface water quality standard – 0.000025 mg/L) with an attenuation factor of 10 applied. The application of the attenuation factor is consistent with Buchman (1999), where the Coastal Protection and Restoration Division of the National Oceanic and Atmospheric Administration uses 10 times the applicable AWQC for screening for dilution and attenuation. The Hawaii chronic saltwater surface water quality standard of 0.000025 mg/L, however, is based on an outdated USEPA criterion. This value appears in “Ambient Water Quality Criteria for Mercury” (USEPA, 1985), and was derived using the

Final Residue Value procedure described in that document. Since the publication of the Great Lakes Aquatic Life Criteria Guidelines in 1995 (60FR15393-15399, March 23, 1995), USEPA no longer uses the Final Residue Value procedure for deriving AWQCs for new or revised 304(a) aquatic life criteria.

DISCUSSION OF STUDY UNCERTAINTY

A summary of uncertainties associated with the analytical data and chemical forms of mercury follows. Estimates of exposure and risk are always subject to a number of uncertainties that could lead to underestimates or overestimates of risks. Because of the conservative nature of the assumptions used in establishing risk-based criteria, it is more likely that risks have been overestimated.

Analytical Data

Some uncertainty associated with the analytical data is expected due to variability in sample matrices and limitations of the analytical methods. Uncertainty due to sample heterogeneity is minimized with careful sample preparation and monitored with replicate sample analyses. Some variability, however, especially for solid samples, is unavoidable.

Under most circumstances, sufficiently sensitive reporting limits (i.e., reporting limits lower than the applicable standards) were achieved. However, in some cases the applicable criteria (specifically, the fish consumption standard and the chronic marine habitat standard) are below the reporting limit for SPLP mercury. The laboratory MDL, however, was less than the criteria in each of these cases. Concentrations between the MDL and the reporting limit cannot be accurately quantified and are considered estimates. Even so, USEPA defines the MDL (determined statistically from multiple analyses of a sample in a given matrix containing the analyte of interest) as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. Since no mercury was detected above the MDL in any of the concrete sample SPLP leachates, it is reasonably certain that mercury was not present in these samples.

Chemical Form of Mercury

Inorganic mercury entering marine and freshwater environments can remain dissolved in the aqueous phase, resorb directly onto soil or sediment, or be chemically altered into either of two more toxic organic forms: methylmercury and dimethylmercury. Of these two forms, methylmercury is of greater environmental concern because of the biomagnification (increasingly higher concentrations) through food webs to levels that are toxic to fish and wildlife, and subsequently, humans.

Because no mercury was detected in any of the concrete sample leachates, it is unlikely mercury mixed with concrete would be converted to methylmercury in a marine environment at concentrations that would cause significant environmental impact.

STUDY CONCLUSION AND PERMIT LIMIT REVISION

This study demonstrated that, even in cases where SPLP mercury in the raw fly ash exceeds AES Hawaii's Solid Waste Management Permit (SWMP) limit, no detectable mercury is leachable from the final concrete product containing such fly ash. As such, mercury in fly ash used as an admixture in concrete (up to 90 percent cement replacement) does not appear to pose a health risk to humans or the environment. Based on these results, and the fact that the current SWMP limit is derived from a chronic saltwater criterion calculated using an outdated method, it was concluded that the SWMP limit for SPLP mercury in the raw fly ash used in concrete products was overly conservative and should be re-evaluated by HDOH.

As noted previously, the basis for the current permit limit was USEPA the chronic marine AWQC accordingly in 2002 of 0.000025 mg/L. The current chronic marine AWQC value of 0.00094 mg/L (USEPA, 2004b) and chronic freshwater AWQC value of 0.00077 mg/L are higher than current chronic freshwater standards promulgated by HDOH. The HDOH 2005 freshwater chronic aquatic habitat goal (based on the Hawaii chronic freshwater surface water quality standard) is 0.00055 mg/L. Thus, AES Hawaii proposed to HDOH at the conclusion of the study that the dilution attenuation factor of 10 be applied to the current HDOH 2005 freshwater chronic aquatic habitat goal of 0.00055 mg/L, thereby resulting in an increased SPLP mercury permit limit from 0.00025 mg/L to 0.0055 mg/L for fly ash when mixed with cement to form concrete and/or flowable fill. This proposed value would be more conservative than that based on USEPA's standards, and would adopt a current standard as the basis for the mercury limit.

HDOH agreed to consider SPLP concentrations below 0.0055 mg/L (0.00055 mg/L with a dilution attenuation factor of 10 applied) to be acceptable for reuse of fly ash in concrete, and that SPLP concentrations below this level would not require confirmation testing or further risk evaluation. HDOH's acceptance of the study results and recommendations therefore effectively resulted in an increase to allowable fly ash mercury limits when used as a concrete additive.

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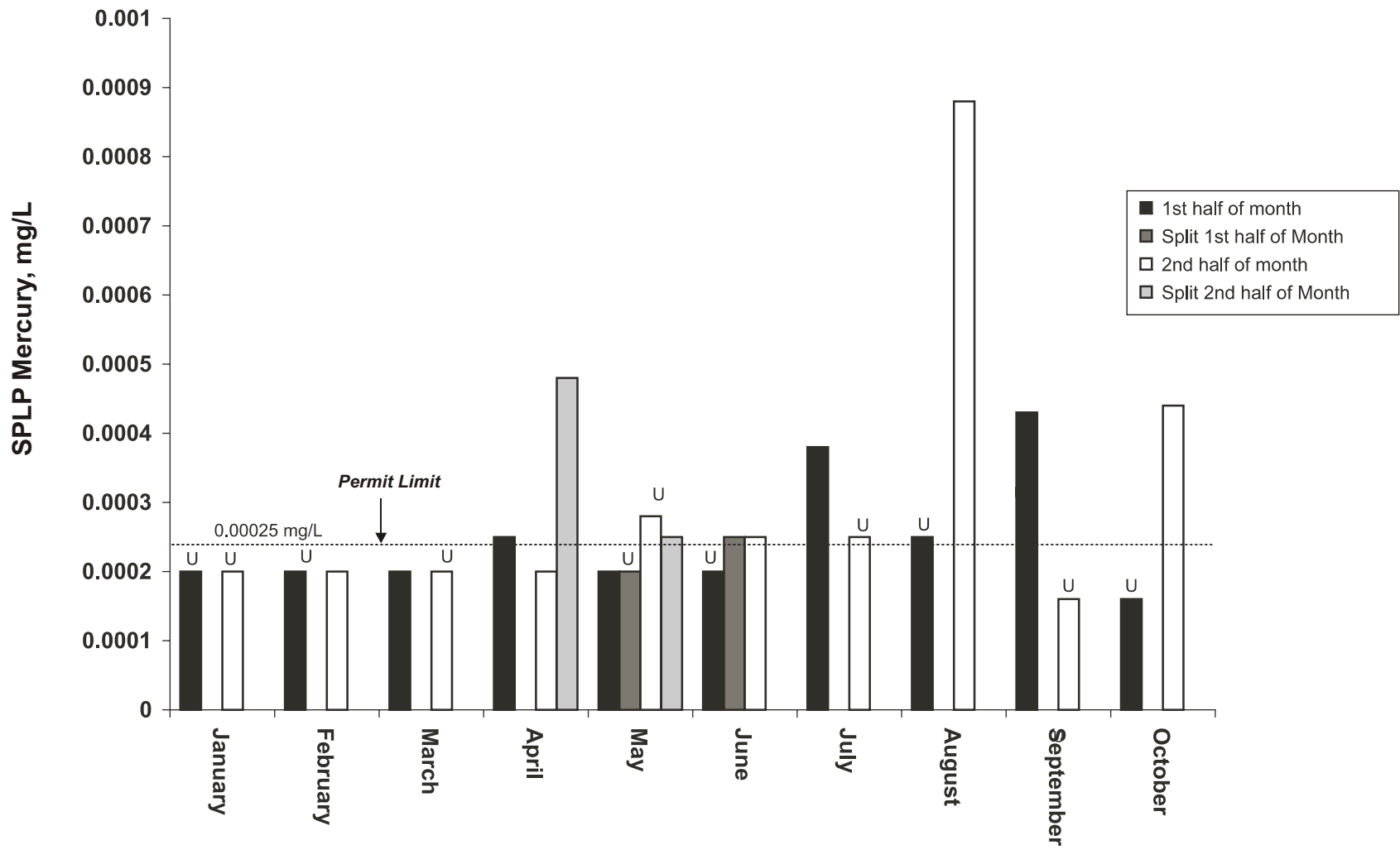
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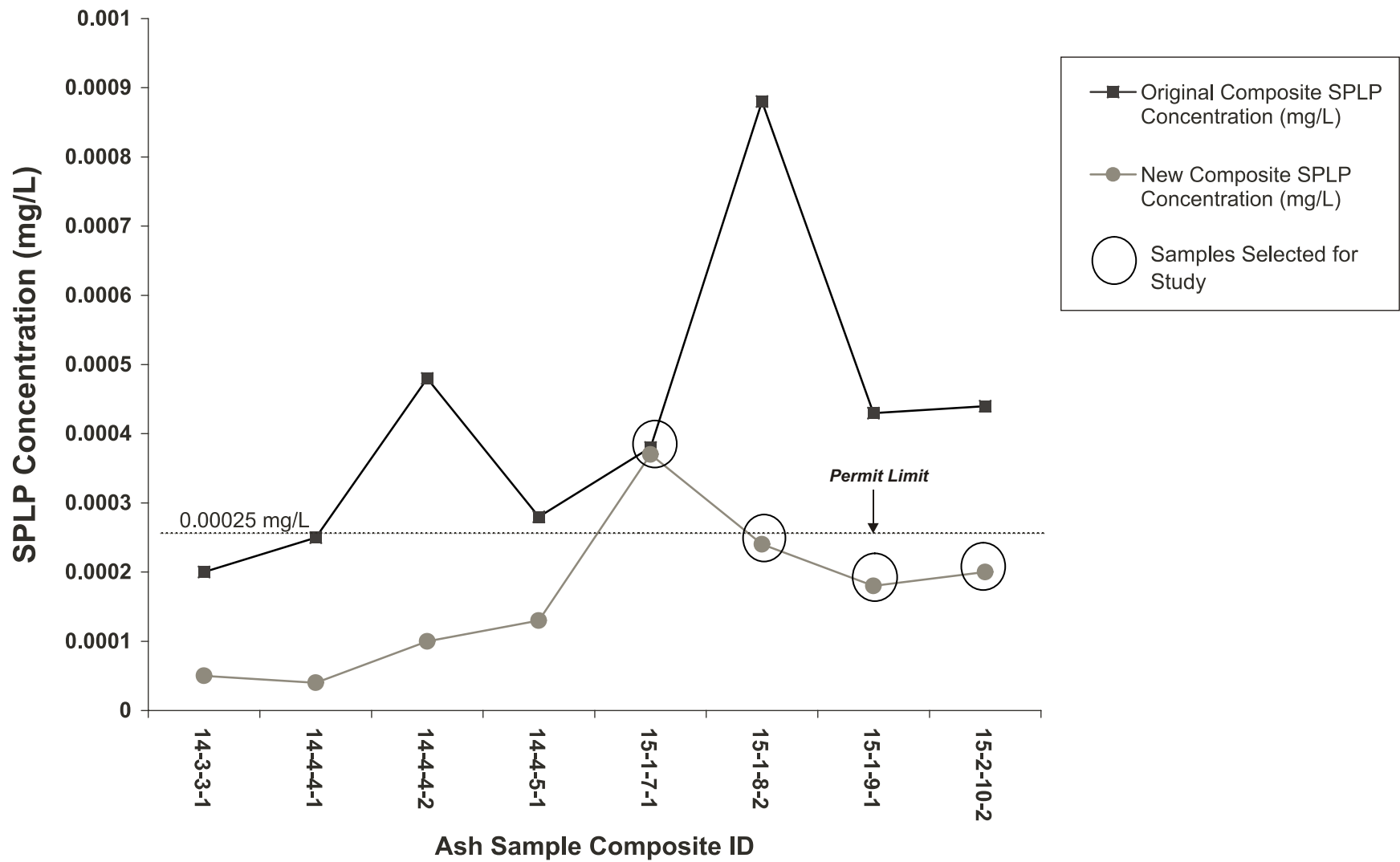
**JANUARY-OCTOBER 2005
FLY ASH SPLP MERCURY RESULTS**

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FIGURE 1



**BASELINE ASH SPLP MERCURY
COMPOSITE SCREENING RESULTS**

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FIGURE 2



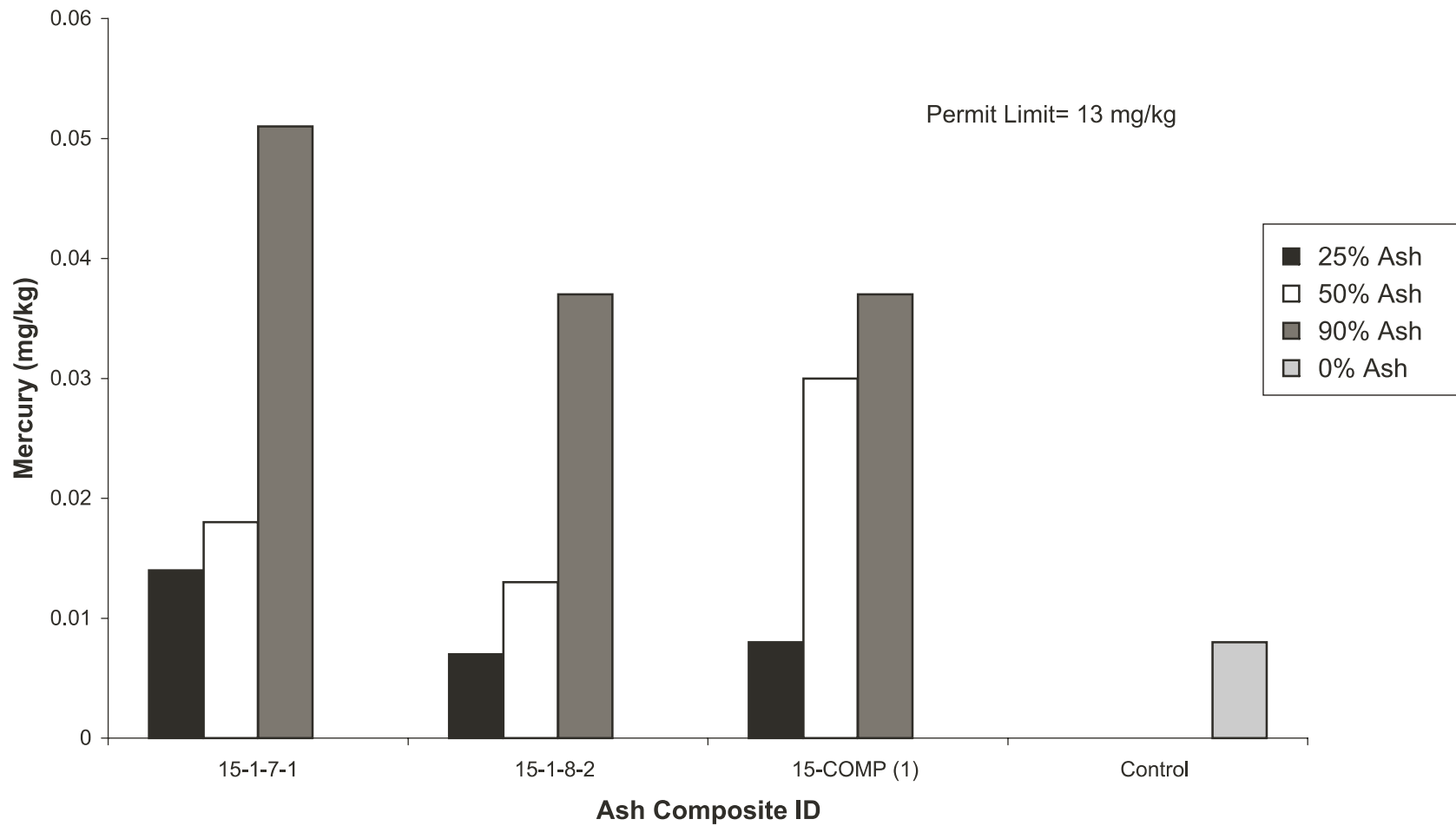
CYLINDER PREPARATION

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URS

FIGURE 3



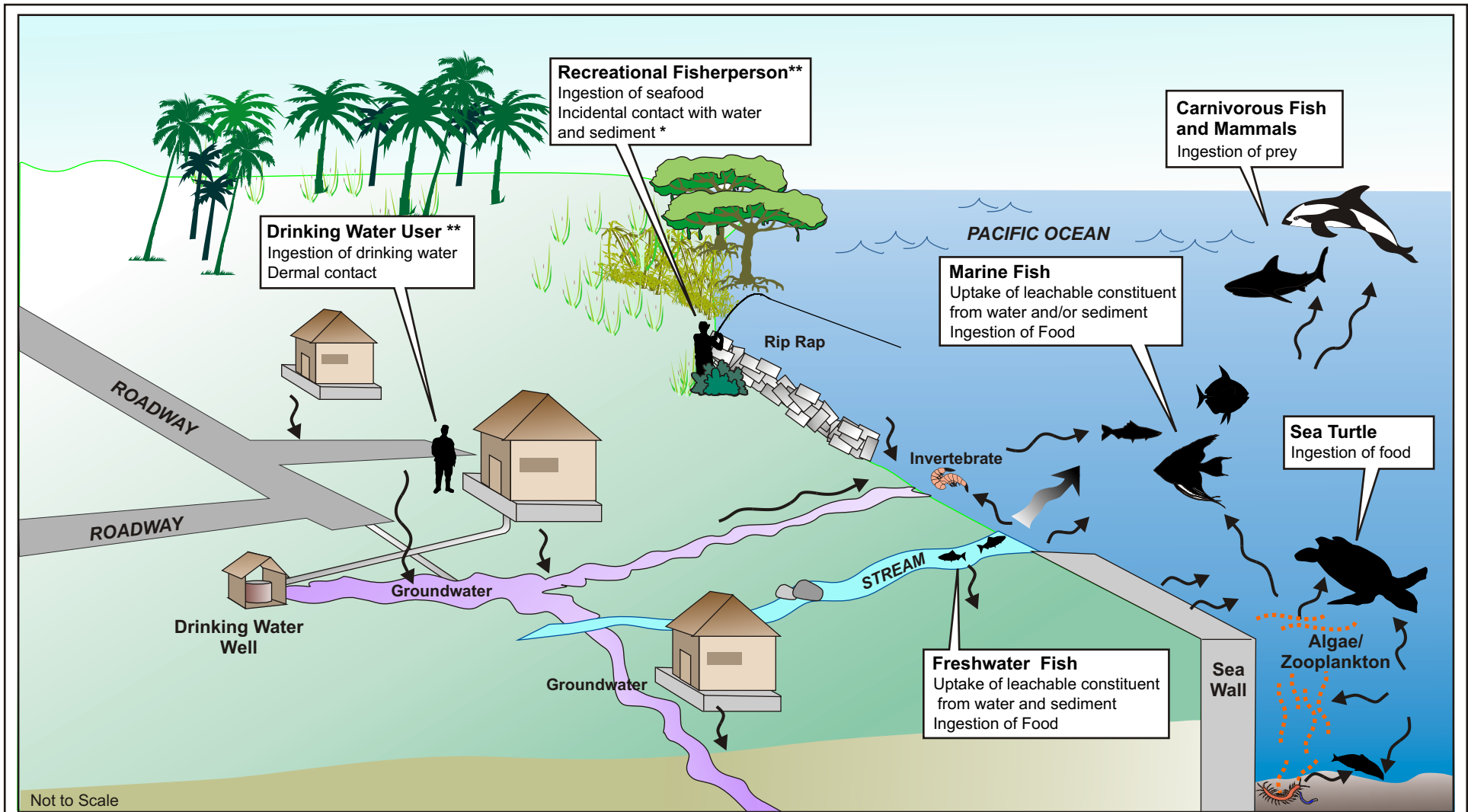
**TOTAL MERCURY RESULTS FOR
CONCRETE MADE WITH FLY ASH (mg/kg)**

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FIGURE 4



LEGEND

→ Leachable Constituent

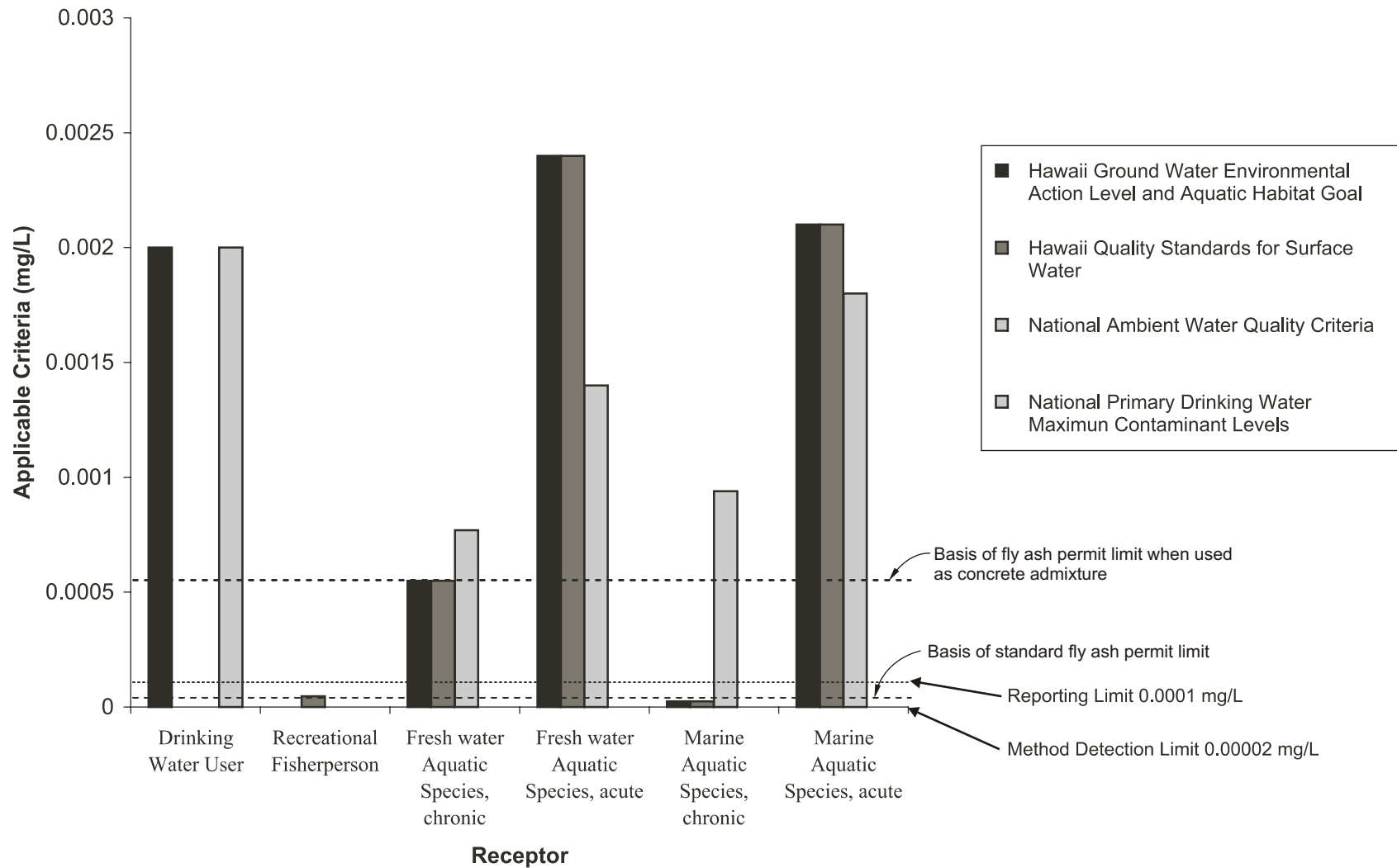
SITE CONCEPTUAL MODEL

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FIGURE 5



All samples were reported as non-detect at an MDL of 0.00002 mg/L

COMPARISON OF SPLP MERCURY RESULTS FROM CONCRETE MADE WITH FLY ASH TO APPLICABLE STANDARDS

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FIGURE 6