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# Using Linear Anionic Polyacrylamide (LA-PAM) to Reduce Water Seepage from Unlined Water Delivery Canal Systems

Michael H. Young Jeffrey J. Tappen Glenn C. Miller Sandra Carroll Richard B. Susfalk

March, 2007

DHS Publication No. 41226

#### Prepared by

Desert Research Institute, Las Vegas, NV University of Nevada, Reno, NV Desert Research Institute, Reno, NV

*In cooperation with* U.S. Bureau of Reclamation

*Prepared for* U.S. Bureau of Reclamation Cooperative Agreement 04-FC-81-1064

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## **EXECUTIVE SUMMARY**

Linear anionic polyacrylamide (LA-PAM) is currently being considered for use as a technology for controlling seepage in unlined canals, and can potentially reduce uncontrolled loss of water from these water delivery systems. Because of this potential use as a water-saving technology, wide interest has been expressed for using LA-PAM in canals in many areas of the 17 western States, particularly in those regions where water is a limited resource. Although this technology is currently being used by some water managers, the risks associated with use of LA-PAM in this particular application have not been completely assessed. Other forms of PAM have, however, been used extensively in drinking water systems for removal of particulates, in cosmetics as thickeners, and in waste water treatment for enhanced settling of precipitated metals, among other uses. Polyacrylamide use in drinking water and waste water treatment systems is governed by the U.S. Environmental Protection Agency (EPA) and states, which regulate the dosage and acrylamide (AMD) content in accordance with use-specific assessments of risk. In the case of LA-PAM usage in canals, no risk assessment or risk characterization has previously been conducted upon which permanent limits can be developed.

As a result of a literature review and after an evaluation of the preliminary data obtained from application in test canals, the following potential risks associated with the use of LA-PAM were identified: (1) ecological and human health impacts associated with the environmental release of residual AMD and (2) the physiological impacts on benthic organisms of LA-PAM release into receiving streams.

Acrylamide is a known cumulative neurotoxin and a suspected human carcinogen. Based on an AMD concentration of 0.05 percent in the polymer and LA-PAM at a typical use level of 1 ppm (1 mg/L), the AMD drinking water standard has been set at 0.5 ppb (0.5  $\mu$ g/L). Though application of LA-PAM in canals is expected to be used in similar or slightly higher concentrations than the drinking water standards, LA-PAM applications will occur only one to two times per year at a rate of no more than 10 pounds/canal acre (lbs/ac) per application. AMD would be released only during the application period. In most drinking water treatment applications, PAM is added continuously.

The largest expected concentration of AMD in water delivery systems occurs when dry LA-PAM is added to dry soil in the canal, followed by the flushing of the canal with irrigation water. Under this application method, LA-PAM concentrations in canal water might be higher than allowed under the safe drinking water standards, but only for brief periods of time (on the order of hours), if at all. This pulse is transient and is expected to dilute as the water is transported through the canal systems. Given the large size of the LA-PAM molecule when hydrated, LA-PAM is not expected to migrate through soil material or into groundwater aquifers. When LA-PAM is applied to a flowing canal as specified by the application protocols currently being developed by the U.S. Bureau of Reclamation (USBR) and the Research Consortium (RC), the maximum AMD concentration is expected to be below the 0.5  $\mu$ g/L drinking water standard. Using these protocols during controlled field experiments (i.e., dry LA-PAM was applied to a water-filled canal at an approximate rate of 10 lbs/ac), AMD concentrations measured in canal water have, to date, remained below 0.50  $\mu$ g/L for all but two samples, out of 35 samples analyzed to date. Most samples (23 of 35) had concentrations less than 0.25  $\mu$ g/L. Though this "dry on flowing" field application does

not encompass all possible application methods, it is commonly used by stakeholders. Nonetheless, only limited information on AMD concentrations is presently available, so only a risk characterization can be provided at present.

The risk characterization contained in this report focused on two potential pathways for AMD exposure as a result of using LA-PAM: ingestion and inhalation. Ingestion of AMD was considered to be the more probable exposure pathway, and would most likely occur through the consumption of (1) canal water immediately after LA-PAM treatment and/or (2) groundwater impacted by AMD. AMD has a very low volatilization potential when dissolved in water and thus does not pose a health risk by way of the inhalation route. Dermal exposure of LA-PAM is not considered given the availability and the recommended use of personal protective equipment by workers applying LA-PAM. Although this document does not address occupational exposure to AMD as a result of applying the LA-PAM per se, it is recommended that personnel use protective equipment (e.g., dust masks) to reduce exposure to airborne particulate LA-PAM containing AMD during the application process.

As part of the risk characterization, AMD concentrations in treated water were calculated based on realistic canal geometries, flow characteristics, and conservative assumptions about LA-PAM hydration and AMD release rates. In addition, concentrations of acrylamide were monitored in treated canals. AMD concentrations in treated waters were compared to current U.S. EPA drinking water standards, and to concentrations derived from the lowest doses that caused adverse effects in animal studies of AMD toxicity, as well as to concentrations equivalent to the highest doses that caused no adverse effects in these studies. The effects of AMD on laboratory animals were extrapolated to humans by applying an uncertainty factor (UF) to the animal doses to account for uncertainty inherent in assuming that sensitive human receptors would respond in the same fashion as animals, and for extrapolating less than lifetime exposures to lifetime exposures. The uncertainty factor of 1,000 used by the U.S. EPA for the chronic acrylamide oral reference dose (RfD) was applied for this exercise (U.S. EPA, 1988). Analytical results of samples collected in operational canals during controlled field experiments indicate that observed concentrations were 50 percent below drinking water standards, approximately three orders-of-magnitude below the UF-adjusted lowest daily doses that caused reproductive impacts in laboratory animals, and about one-fourth of the drinking water concentration associated with a one-inten thousand lifetime risk for cancer if consumed over a lifetime according to the U.S. EPA.

Based on the knowledge gained from field and laboratory experimentation, and assuming that LA-PAM is applied in accordance with the draft application protocols proposed by the Research Consortium, the following conclusions were made:

 The concentration of LA-PAM could, for brief periods of time during field application, exceed the Safe Drinking Water Act treatment technology limitation of 1 mg/L polymer. Concentrations of AMD are likely to remain below the drinking water treatment technology standard 0.5 μg/L monomer from a certified polymer. To date, of 35 water samples collected and analyzed during field experiments, 18 were below 0.1 μg/L of AMD, 14 were below 0.5 μg/L, and two were above 0.5 μg/L and less than 0.7 μg/L. Studies being conducted in the laboratory indicate that incipient AMD in the LA-PAM formulation degrades relatively rapidly in the environment, and does not accumulate/bioaccumulate, and no AMD is formed in significant amounts from breakdown of the polymer in the environment.

- 2. Elevated concentrations of LA-PAM and AMD are expected in surface water samples immediately after LA-PAM addition to a canal, and in close proximity to the locus of addition. These elevated concentrations will be transient and depend on the application time (<1 to 12 hours) in a specific reach of a canal being treated. It is expected that this condition will occur only one to four times per year.
- 3. The highest concentrations of AMD expected (based on limited field data) are nearly two orders of magnitude below the No-observed-adverse-effect-level (NOAEL) for human receptor surrogates. Consequently, little effect is expected for AMD, from an ecotoxicological perspective.
- 4. The highest LA-PAM concentrations expected will be in canal sediments. Effects of LA-PAM usage on benthic organisms associated with LA-PAM usage are still being investigated through field experiments, but preliminary results show elevated benthic organism drift rates for about 11 hours after PAM addition; other impacts to benthic communities are still being examined. Until these research findings are completed, LA-PAM use should be avoided near biologically sensitive canal systems.
- 5. Depending on the assumptions used in calculations, and using the results collected in full-scale canal tests, the predicted concentrations of AMD in canal water will remain close to or below the drinking water standard ( $0.5 \mu g/L$ ). Furthermore, field samples collected to date have contained AMD at concentrations consistently lower than the predicted concentrations. Human exposure of AMD from ingestion of canal water is low, and exposure from potential groundwater contamination would be progressively less. Even if AMD could reach groundwater systems from the transient pulse of AMD in the canal, concentrations of AMD would be below levels observed in canal water, and would be further diluted in groundwater as it moves.
- 6. Additional information on the environmental fate of AMD and LA-PAM is necessary for a comprehensive risk assessment of the use of LA-PAM for seepage control, especially as it relates to degradation pathways for AMD in the ambient and groundwater environment.
- 7. Though the findings by Manson *et al.* (2005) (see Sections 2.2.2.2 and 2.2.2.3) have significant bearing on the use of LA-PAM in canals, the exposure analysis conducted in this report indicates that acute (short-term) AMD concentrations in canal waters will be between one and four orders of magnitude below the chronic (long-term) levels needed to impact human health.

The U.S.EPA is presently preparing an updated health risk assessment for acrylamide as part of the Agency Integrated Risk Information System (IRIS) program. The existing IRIS assessment was completed in 1988. Since that time a number of new studies of the cancer and noncancer health risks associated with exposure to AMD have been published. These studies will be included in the new IRIS Toxicological Review for Acrylamide. Agency estimates that the updated assessment will be peer reviewed in December of 2007 (http://cfpub.epa.gov/iristrac/index.cfm); it will be made publicly available prior to the peer review.

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Contexts do not reflect the views of this agency.

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# LIST OF ACRONYMS AND DEFINITIONS

- ATSDR Agency for Toxic Substances and Disease Registry, a branch of the Centers for Disease Control and Prevention of the U.S. Department of Health and Human Services.
- AMD acrylamide, the primary monomer used to prepare anionic, nonionic, and cationic polyacrylamide polymers.
- bw body weight (mass).
- pound/canal acre (lbs/ac) a unit of application, measured as pounds of material used to cover an acre of wetted area in the canal, as determined by product of the wetted perimeter and lineal distance along the canal.
- Canal For the purposes of this risk characterization, a water delivery system used to convey or deliver water from point A (e.g., reservoir or river) to point B (agricultural field, reservoir or river) that is unlined on the bottom (hence with an earthen subbase), and open to the atmosphere at the top.
- DRI Desert Research Institute, located in Reno and Las Vegas, NV. DRI is governed by the Board of Regents, and is a branch of the Nevada System of Higher Education.
- LA-PAM For the purposes of this report, the acronym for linear anionic polyacrylamide. This new acronym is being used to avoid confusion between the formulation of PAM being discussed in this report–as defined below–and the wide variety of other PAM formulations that could be applied in canals. LA-PAM refers to a specific group of compounds.
- LOAEL Lowest-observed-adverse-effect level is defined as the lowest tested dose of a substance that has been reported to cause harmful (adverse) health effects in people or animals. (Source: http://www.atsdr.cdc.gov/glossary.html).
- MCL Maximum Contaminant Level The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCLGs as feasible using the best available treatment technology and taking cost into consideration. MCLs are enforceable standards.
- MCLG Maximum Contaminant Level Goal The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are non-enforceable public health goals.
- MW Molecular weight.
- NOAEL No-observed-adverse-effect level is defined as the highest tested dose of a substance that has been reported to have no harmful (adverse) health effects on people or animals. (Source: http://www.atsdr.cdc.gov/glossary.html).
- PAM Anionic polyacrylamide formed either by free radical copolymerization of acrylamide and acrylic acid (or sodium acrylate) or by hydrolysis of polyacrylamide formed by the free radical polymerization of acrylamide. This report restricts PAM to: 1) formulations that are certified to conform to National Sanitation Foundation / American National Standards Institute NSF/ANSI Standard 60; 2) be linear (not deliberately branched); 3) be anionic with an approximately 30 percent (mole %) charge density; 4) have a high molecular weight between 12 and 24 Mg/mole; and 5) contain no more than 0.05 percent acrylamide monomer, by weight, of the active polymer content. In this report, we use LA-PAM when referring to PAM with these characteristics.

- PRP Peer Review Panel, the PAM Peer Review Panel or Committee that is reviewing approaches and results from the PAM research program being conducted by the Research Consortium.
- RC Research Consortium means, collectively, the Desert Research Institute, University of Nevada, and U.S. Bureau of Reclamation.
- Reference Dose (RfD) A numerical estimate of a daily oral exposure to the human population, including sensitive subgroups such as children, that is not likely to cause harmful effects during a lifetime (<u>http://www.epa.gov/ocepaterms</u>). RfDs are generally used for health effects that are thought to have a threshold or low dose limit for producing effects.
- TT Treatment Technique A required process intended to reduce the level of a contaminant in drinking water.
- USBR United States Bureau of Reclamation, an entity of the federal government.
- U.S. EPA United States Environmental Protection Agency, an entity of the federal government.
- UNR University of Nevada, Reno, which is governed by the Board of Regents for the Nevada System of Higher Education.
- WHO World Health Organization.

# 1.0 INTRODUCTION

## 1.1 Scope of Linear Anionic Polyacrylamide (LA-PAM) Risk Characterization Report

The purpose of this document is to describe potential ecological and human health risks from exposure to linear anionic polyacrylamide (LA-PAM) and its residual monomer, acrylamide (AMD), when LA-PAM is used in canals to reduce seepage. The risk characterization presented in this interim report is based on a literature survey of previously published findings and preliminary field data from ongoing research projects. Previous risk assessments considered PAM usage in many environments of interest, but not in canals. The lack of scientific studies of LA-PAM behavior in canal systems led the United States Bureau of Reclamation (USBR) to initiate the LA-PAM research program and the associated risk characterization.

Research being conducted under this program by a Research Consortium (RC) of government and university researchers is meant to augment the existing dataset of LA-PAM behavior in canal environments by addressing specific questions posed by a diverse group of outside scientists from university, government, and industry, and by stakeholders in the end-user community. The questions were posed through a series of meetings held in Denver, CO, and Reno, NV, during late 2004 and early 2005. The questions were further vetted and refined by an independent PAM Peer Review Panel (PRP), which was organized by the Research Consortium in April 2005. The final set of questions is presented in Section 1.4 and forms the guiding pathway for the research being conducted on LA-PAM. The research emphasizes the fate and transport of LA-PAM and AMD in the canal environment, and the characterization of ecological risk from LA-PAM applications.

Also, for the purposes of this report, the scope of the document is limited to LA-PAM and AMD and not to the other impurities that could be contained in other commercial PAM products. This decision was justified based on the requirement that any PAM products used to reduce seepage be certified as acceptable for drinking water treatment against ANSI/NSF Standard 60. The inclusion of AMD in the Risk Characterization is consistent with the regulatory emphasis placed on acrylamide monomer when the polymer is used in drinking water treatment applications.

The current research program was initiated in 2005, and is examining a diverse set of field, laboratory, and numerical studies to better understand LA-PAM usage and risks. Field experiments were conducted at several locations throughout the water year, some at operational canal systems. Data from these field experiments are still being compiled and analyzed, and will be published as technical reports in early 2007. Laboratory experiments have been designed to better understand basic biophysical processes that govern fate and transport of LA-PAM and AMD in water and soil systems. Specifically, the Research Consortium is examining LA-PAM hydration and AMD release rates into the aqueous phase, biotic and abiotic degradation pathways of LA-PAM/AMD, and the efficacy of LA-PAM to reduce seepage as functions of water chemistry. Similar to the situation with field experiments, experimental results are yet to be completed and are not included directly in the present risk characterization.

# 1.2 Hazard Assessment of LA-PAM Use

Linear anionic polyacrylamide is a high molecular weight, water soluble compound comprised of repeating units of AMD and acrylic acid monomers. Polyacrylamide has been used for numerous applications—as a soil conditioner, in wastewater treatment, in water treatment, in the cosmetic, paper, mining, and textile industries, and in the laboratory as a solid support for the separation of proteins by electrophoresis (Friedman, 2003). Although several types of PAM are available, (anionic, cationic, nonionic, linear, cross-linked) and they are available in different forms (dry [powder, flake or granule]; liquid emulsion or dispersion), only dry, LA-PAM is the form currently being considered for routine use to reduce seepage losses from canals. Linear anionic polyacrylamide appears to be effective for partially sealing canals under the right field conditions. Similar forms of PAM have been used extensively in furrow irrigation applications to reduce soil erosion, and in settling ponds at construction site storm detention basins (CalTrans, 2004); however, this use of PAM is relatively new, and the addition of LA-PAM to canals can result in the release of residual products (i.e., AMD) into the environment, and potentially into drinking water systems. This characterization document only considers the risk to humans and to the environment from using LA-PAM in dry form for seepage control.

Although PAM is generally considered to be relatively nontoxic to humans and animals (i.e., Cosmetics Ingredient Review Safety Panel [1991] Andersen [2005] reported on nonionic forms), the ecological risks associated with the use of LA-PAM in water delivery canal systems are not well studied. Because LA-PAM can potentially have an effect on sediments and the associated benthic life, as well as direct impacts on aquatic life, this risk characterization considers the current literature and new information on how LA-PAM affects aquatic systems.

The primary concern of using LA-PAM for seepage control is how AMD could be released, potentially affecting human health and the environment. Acrylamide is a small but reactive molecule that has been used during the last 50 years for the production of PAM polymers. Acrylamide is released in small amounts wherever PAM is used (von Muhlendahl and Otto, 2003). The effects of AMD in cells, tissues, animals, and humans have been studied extensively; relevant findings are discussed below.

# 1.3 Why is Acrylamide a Concern?

Acrylamide is a known animal carcinogen (Hellenäs and Abramsson-Zetterberg, 2005; Manson *et al.*, 2005; Thulesius and Waddell, 2004) that has received recent increased focus due to the discovery of its occurrence in certain cooked foods. Acrylamide is formed when foods containing the amino acid asparagine are cooked at a relatively high temperature (Amrein *et al.*, 2004). When looking for the source of high internal levels of the acrylamide adduct to hemoglobin in occupationally exposed persons in Sweden, diet was identified as the probable source (von Muhlendahl and Otto, 2003). Hemoglobin adducts are commonly used as a biomarker for human acrylamide exposures.

Since this initial observation, the background levels of acrylamide in the environment have been a focus of research and public discussion (Taeymans et al., 2005). Acrylamide, and its metabolite glycidamide, are mutagenic *in vivo* to somatic cells and germ cells. The World Health Organization (WHO) and the U.S. EPA classify acrylamide as a probable carcinogen in humans (WHO, 2006; U. S. EPA, 1988). WHO has estimated that the intake of

acrylamide is 0.3 to 0.8  $\mu$ g/kg body weight per day for the average person (von Muhlendahl and Otto, 2003), and this exposure is almost entirely from foods. Acrylamide is also a component of tobacco smoke, and presumably also formed via burning of other plant material (European Commission, 2002).

For the general population, nonfood- and nontobacco-related exposures to AMD include exposure to the residual monomer in PAM, albeit much smaller exposure than in some foods. The largest use of PAM is as a flocculant for clarifying drinking water and for treating municipal and industrial wastewater. Other major uses are as flow control agents in oil-drilling processes, binders and retention aids in the pulp and paper industry, for soil stabilization, and in cosmetics and toiletries. Acrylamide polymerization has been used *in situ* in the formulation of some grouts for construction and repairing of sewers and tunnels.

For the acrylamide aspect of this risk characterization, the project team has investigated the potential exposure of humans and the environment to AMD from LA-PAM usage in canals, and whether this potential exposure poses a significant risk.

## 1.4 Risk Characterization Objectives

The risk characterization objectives were defined during a series of technical meetings of scientists from government, university, end users, and industry. The set of seven research questions central to risk characterization were developed and finalized by the USBR, Desert Research Institute (DRI), and University of Nevada, Reno (UNR).

- 1. What are the ecological and human health risks of the use of PAM and AMD when used in unlined canals for seepage control?
- 2. Does PAM (the polymer) degrade to the monomer, acrylamide (AMD)? If so, does the amount present a significant risk for contamination of surface water or groundwater?
- 3. What is the relative significance of residual AMD in the original polymer versus AMD as a PAM degradation product (if it is generated)? Are there other potential or known degradation products of PAM that are of toxicological concern?
- 4. What is the fate (including biodegradation) and transport of AMD (and/or PAM, and product components) in surface water, soil, and groundwater systems? What data gaps exist specific to this application?
- 5. How do field application practices (e.g., application of PAM to dry soil versus water in a flowing canal) affect the risk of use of PAM? What field practices can be used to reduce risks associated with PAM application?
- 6. If residual PAM is released into receiving water, what are the ecological risks and issues associated with PAM in surface water (e.g. armoring channel morphology, bioaccumulation, etc.)?
- 7. Are there any other issues regarding the human and ecological risk of use of PAM that should be considered?

# 2.0 CHEMISTRY, TOXICOLOGY, AND EXPOSURE: POLYACRYLAMIDE AND ACRYLAMIDE

## 2.1 Polyacrylamide (PAM)

### 2.1.1 Chemical and Physical Properties of PAM

Free-radical polymerization of AMD in the presence of various amounts of acrylic acid generates anionic PAM, and the polymer has entirely different chemical and biological characteristics than the monomer. Whereas AMD is a reactive species primarily due to the double bond, polymerization eliminates the double bond, and renders LA-PAM relatively chemically inert under normal conditions. While the amide group of PAM can undergo hydrolysis to yield ammonia and the corresponding carboxylic acid, PAMs are not readily prone to nucleophilic addition across the backbone, since they now possess only single carbon-carbon bonds. The large molecular size of LA-PAM (high molecular weight) reduces its ability to be absorbed and, therefore, its toxicity to humans and animals through ingestion or contact.

The molecular weight (MW) of linear forms of LA-PAM in the marketplace varies from about 1.0 to about 20 million grams per mole (g mol<sup>-1</sup>) although lower molecular weight versions may be used in specialized industrial applications. Anionic PAMs are usually at the higher end of this range while cationic PAMs are at the lower end. The classification of molecular weight is relative and, therefore, the coagulant and flocculant polymer industry has developed an informal but widely used classification system, which is shown in Table 1 (Barvenik, 1994). The extent of anionic sites along the PAM chain, also called the charge density or frequency, is controlled by controlling the ratio of AMD and acrylic acid (or sodium acrylate) present during polymerization. Although there are some specialized industrial applications or an occasional water or wastewater treatment application where anionic PAMs of lower or higher charge density are most effective, anionic PAMs of 20 to 30 percent charge density are most effective in the great majority of anionic PAM applications, particularly those involving flocculation of soil fines. Accordingly, anionic PAMs of 20 to 30 percent charge density have most often been used in canal seepage control.

Classification	${ m Mass}^\dagger$
Low MW	<10 <sup>5</sup>
Medium MW	$10^5 - 10^6$
High MW	$1-5 \ge 10^6$
Very High MW	$>5 \text{ x } 10^6$

 Table 1.
 Molecular weight (MW) classification system of water-soluble polymers in the marketplace.

†- mass shown is in grams per mole (g mol<sup>-1</sup>)

### 2.1.2 Chemical Stability of PAM

Caulfield *et al.* (2003a) found that linear PAM was stable at room temperature and when subjected to continuous exposure to fluorescent light. When heated to 95°C, the PAM carbon–carbon backbone was stable and did not release any detectable AMD after 15 days. The thermal degradation of PAM is influenced by a number of factors including MW, copolymer composition, mode of synthesis, oxygen content, thermal history, and the presence of impurities (Caulfield *et al.*, 2003a). However, it has been suggested that there are certain common temperature regions where thermal degradation primarily occurs. The thermal aging of PAM can therefore be divided into three regions depending on the temperature: the first, below about 200 °C, the second, between approximately 200 and 300 °C, and the third above 300 °C (Caulfield *et al.*, 2003a).

Polyacrylamide was found to release small amounts of AMD monomers under highenergy ultraviolet (nonenvironmental) 254-nm irradiation. However, the released amount was approximately 50 parts per million (ppm) of monomer units after 10 days exposure and was sufficiently low to conclude that PAM did not break down, releasing free AMD under the UV irradiation conditions. A drop in viscosity was also observed (Caulfield *et al.*, 2003b). Polyacrylamide photodegradation is largely a free-radical process that can lead to cleavage of the polymer backbone (bond scission), cross-linking, introduction of new functional groups including unsaturation, and the formation of lower molecular weight products. These irreversible changes are responsible for the observed loss of chemical and physical properties of the polymer.

Wan *et al.* (2005) investigated the stability of medical PAM hydrogel *in vitro*, because this form of PAM has been used in plastic and aesthetic surgery in China, Ukraine, and Russia for more than 10 years. In these cases, hydrogen peroxide (3 percent by volume) was added to PAM, and AMD concentrations in the supernatant, as determined by high-performance liquid chromatography at 0.5, 1, 2, and 3 hours after oxidizing PAM, were 12.7  $\mu$ g/L, 13.5  $\mu$ g/L, 103  $\mu$ g/L, and 274  $\mu$ g/L, respectively. The beginning concentration (T<sub>0</sub>) of AMD in the supernatant of PAM hydrogel was 7.7  $\mu$ g/L, suggesting that PAM was degraded to AMD by the hydroxyl radicals produced through the introduction of H<sub>2</sub>O<sub>2</sub> (though it is noted that the response of hydrogel to hydrogen peroxide could be different from that of a linear polymer). Under the same conditions, Wan *et al.* (2005) found that the AMD content was stable, suggesting that AMD can exist for some time in the presence of this oxidant. The use of 3 percent hydrogen peroxide in medical application experiments is extreme relative to environmental conditions, and no data were found that indicates that AMD is produced from PAM under environmentally relevant conditions.

Thus, at present, research findings indicate that the only relevant source of AMD in the environment from LA-PAM applications in canals appears to be from residual (<0.01% to 0.05%) AMD in the LA-PAM products, released as the LA-PAM hydrates during dissolution (and use).

#### 2.1.3 LA-PAM and Human Health

Polyacrylamide has received extensive use in direct applications and in products that are closely associated with humans, including drinking water and cosmetics. As such, the toxicology of PAM has been examined previously in a variety of applications. A safety

*Contexts do not reflect the views of this agency.* 

assessment of PAM use in cosmetics (Cosmetic Ingredient Review Safety Panel, 1991) noted the lack of absorption following gavage administration to rats, which was attributed to the inability of PAM to be absorbed in the gastrointestinal tract. In these studies, PAM administration at 500 and 2,000 ppm did not cause adverse effects over a three-generation reproduction study. For cosmetics applications, this study concluded that PAM containing less than 0.01 percent AMD monomer is safe as a cosmetic ingredient as presently used.

As reported by Anderson (2005) in a recent review of polyacrylamide, rats and dogs were treated with polyacrylamide at doses of up to 464 mg/kg body weight/day for up to 13 weeks with no observed adverse effects and were also able to tolerate diets containing up to 5% polyacrylamide for up to two years without displaying significant adverse effects. In an acute study, an oral dose of 4.0 g/kg body weight was without toxicological impact.

Potentially enhanced exposure to airborne PAM by applicators has not been studied for this specific application, although it was reported that occupational exposure at a PAM manufacturing plant to airborne PAM dust at 1 mg/m<sup>3</sup> did not have adverse health effects (reported in the Cosmetic Ingredient Review Safety Panel, 1991).

# 2.1.4 Characterization of Exposure Pathways for LA-PAM

When LA-PAM is used as a sealant technology for canals, as described in this report, three exposure pathways quickly become apparent: dermal absorption, inhalation, and ingestion. For the purposes of this characterization, dermal absorption will not be considered given the recommended use of long-sleeved shirts and/or other personal protective equipment (Tyvek suits, rubber gloves), which will minimize dermal exposure to LA-PAM. Exposure to LA-PAM via the inhalation pathway could be more likely when dry LA-PAM is applied in the canals. A review of the manufacturer's Material Safety Data Sheet for the PAM product used in this study recommends the use of a dust mask when the concentration of dust exceeds 10 mg/m<sup>3</sup>. A review of available literature found only one health effect study on the occupational exposure to PAM (McCollister *et al.*, 1965 [as listed in Andersen, 2005]). That study found no adverse health effects as a result of chronic workplace exposure to PAM at an average concentration of  $1 \text{ mg/m}^3$  of air. At the present time, no data are available on the concentration of PAM in the breathing zone air under the proposed application protocols. Therefore, it would be prudent to minimize potential worker exposure during LA-PAM application through the required use of personal protective equipment (i.e., dust masks).

Ingestion was considered to be the more probable nonoccupational exposure pathway, primarily though the consumption of canal water subsequent to LA-PAM treatment. However, as described by Cosmetic Ingredient Review Safety Panel (1991) and Andersen (2005), data suggest that LA-PAM is not a significant health risk when used as a canal sealant because of the small amounts of LA-PAM that would likely be ingested and because of the low uptake of LA-PAM from the gastrointestinal tract. Furthermore, the general public would not be exposed to LA-PAM from field applications at the levels needed to cause health effects which, as discussed above in Section 2.1.3, were in excess of 400 mg/kg/day based on studies in rats and dogs.

Therefore, for the purposes of this risk characterization, human health impacts from LA-PAM are not considered significant and thus will not be considered further.

### 2.1.5 Ecological Risks of PAM

As discussed previously, only anionic PAM is being used, or proposed to be used, to control seepage in canals. At the present time, the RC is unaware of nonionic or cationic forms of PAM being used. Nonetheless, nonionic and cationic forms of PAM are also available for purchase and thus the potential exists for these forms to be used (either inadvertently or intentionally) in canals.

An ecological-toxicological assessment of six flocculants, including PAM, was done in the course of a study at Lake Baikal, Russia (Beim and Beim, 1994). Flocculant toxic effects on water organisms of various systematic groups were found using international biotesting parameters. The flocculants affected all aquatic ecosystem components and, especially, protococcal algae, invertebrates, and adult fish (Table 2; Beim and Beim, 1994). Comparative biological activity studies for different types of flocculants (cationic, anionic and nonionic) showed that cationic flocculants had the highest acute (lowest LC<sub>50</sub>) and longterm toxicity (Beim and Beim, 1994). Cationic PAM, at the concentrations considered for canals, is generally 10 to100 times greater in toxicity than anionic PAM to most of the organisms studied. According to the complex of pathological effects observed, the PAM flocculants seemed to possess a membrane-binding mode of action that interferes with cellular or tissue function. "Vital" concentrations of flocculants (Table 2) were expressed in algae as cell growth rate and photosynthesis (O<sub>2</sub> production and chlorophyll A content), in *Crustacea* as median fertility, and in fish (e.g., adult minnows) as hematological changes in the content of blood cells (Beim and Beim, 1994). The definition of "vital" concentrations was not provided, although it appears to be the concentration that affects crustacea or other organisms. The toxicity of cationic PAM was also reported by Muir et al. (1997), who showed that, though no bioaccumulation was observed, cationic PAM did bind to the gills of rainbow trout.

	Magnafloc	Sanfloc	PAA	Zetag 64	Sanfloc	Catfloc
Test	E10	N520P			CH009P	
Organisms	(Anionic)	(Nonionic)	(Nonionic)	(Cationic)	(Cationic)	(Cationic)
Saprophytic						
bacteria	10.0	10.0	10.0	10.0	N.D. <sup>††</sup>	N.D.
Algae	0.01	0.001	0.01	0.002	0.00001	0.001
Planaria	1.0	100.0	0.1	0.1	N.D.	N.D.
Gammaridae	10.0	1.0	10.0	0.1	0.01	0.001
Daphnia	0.01	1.0	1.0	0.1	0.000001	0.00001
Minnow	0.5	0.1	0.01	0.002	0.0001	0.0001
Fish roe of:						
Bullhead	10.0	1.0	1.0	0.1	0.1	0.01
Grayling	5.0	1.0	100.0	1.0	1.0	N.D.
Omul	N.D.	10.0	0.1	0.1	0.1	N.D.

Table 2. Values of flocculants vital concentrations (mg/L) for water organisms (from Beim and Beim, 1994).<sup>†\*</sup>

+ - Specific formulations for PAA, Zetag 64 and Catfloc not provided by authors

\* - Detection limits not provided by authors

†† - N.D. is PAM presence at nondetectable concentrations

Data were collected by Grula *et al.* (1994) to examine whether rheological properties of PAM (used in oil recovery operations) were altered because of microbial degradation in either aerobic or anaerobic conditions. Their results indicated that PAM could be utilized as a nitrogen source by several species of *Pseudomonas* isolated from soil, especially in the absence of other N sources (e.g., NH<sub>4</sub>Cl). The level of growth attained was less (~25 to 50%) than that in experiments with NH<sub>4</sub>Cl. Grula et al. (1994) also showed that growth of sulfate-reducing bacteria from treated petroleum wells was stimulated by PAM. In these experiments, the polymer served as both a nitrogen source and electron donor but was not assimilated for carbon (e.g., mixotrophy). It remains unclear however whether or not sulfate reduction or other anaerobic metabolisms, which occur at negative redox potentials, are significant over any portion of the annual wetting cycle in canals or receiving waters.

The response of aquatic biota to LA-PAM exposure is being investigated by the RC by comparing macroinvertebrate communities that are affected and unaffected by PAM treatment in an irrigation canal, and in an experimental array of troughs where their response in control (untreated troughs) and 40 lbs/acre treatments are compared. During a canal treatment in Water Year 2005 of Smith Ditch (experimental conditions discussed below in Section 3.3) using an application rate of approximately 10 lbs/acre, differences between benthic macroinvertebrate (BMI) species richness and community structure, before and following treatment, were not statistically significant, and there were no differences in community tolerance indices before and following PAM (these communities were highly tolerant of harsh conditions with indices for all samples approximately 8). Decreases in the abundance of pond snails (*Physa* sp.) in some treated areas suggested, however, that some BMIs were adversely affected by this PAM exposure. The response to LA-PAM application was also examined by comparing macroinvertebrate drift rates before, during, and after treatment at five sites (spanning approximately 2000 m) located downstream from the treated reach of canal. Differences between species richness before and following treatment were not statistically significant, but richness associated with passage of maximum concentrations was higher at all sites than was observed during pre-LA-PAM samples. Exposure to LA-PAM treatment was a statistically significant factor, however, in an analysis that examined environmental factors that were important to structuring the drifting community. Maximum drift rates observed between five and 11 hours following application were usually several times greater than rates observed during application or before LA-PAM treatment. Copepods, mayflies, and *Physa* sp. were primary species exhibiting elevated drift rates. These studies were not designed to discern the ultimate cause of effects to invertebrates. The minor affect of LA-PAM on the benthic community and characteristics of the drifting community suggest, however, that organisms were redistributed in the canal system rather than being affected by mortality.

The response of riffle dwelling BMIs was examined in an experimental array of troughs with gravel substrates and a community from the Colorado River near Grand Junction, Colorado. Community tolerance values were approximately 6 in control and treatment troughs, indicating that these communities were less tolerant to harsh conditions than communities in Smith Ditch. Comparison of pre- and post-treatment BMI species richness and density in the substrate were not significantly different for control or treatment trials. Species richness and density were lower in substrates treated with LA-PAM than they were in controls. Multivariate analysis indicated that 40 lbs/acre and control communities were different. Differences between control and LA-PAM species richness and drift rates

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were not significantly different, but drift rates were higher in treated trials than in control trials. Blackflies and mayflies were the most active members of the drift. Differences between control and treatment rates were statistically significant for blackflies. Canal and trough experiments both indicate that aquatic macroinvertebrates are affected by LA-PAM. Risks to aquatic communities in canals are comparatively minor because these systems are poor quality, inherently harsh environments that are frequently stressed by drying, dredging, and water management activities. The risk to natural systems can be minimized through application procedures that will prevent the release of LA-PAM into these waters.

Response of *Daphnia magna* to AMD and LA-PAM treatments were investigated in the laboratory experiments as a part of 'impact on receiving waters.' Three treatments of PAM (1, 10 and 100 ppm) and AMD (0.5, 5 and 50 ppb) were used in enclosed containers with *Daphnia* during the period of the experiments lasting up to 30 days. The AMD experiments showed that a few *Daphnia* showed a minor delay or reduction in 2<sup>nd</sup> and 3<sup>rd</sup> clutch sizes whereas their growth, overall reproduction and mortality were generally not affected by the treatments. In the LA-PAM experiment, *Daphnia* did not grow and reproduce well in 1 and 10 ppm concentrations and did not survive 100 ppm very long. From the visual observations, the effect of LA-PAM on *Daphnia* appeared to be more of a physical hindrance than toxicity because *Daphnia*'s movement was abnormal. Also, in these experiments, the continuous exposure of *Daphnia* to LA-PAM would most likely not occur in the receiving waters even if a small amount of LA-PAM were to be transported. However, this is an ongoing study and more experiments need to be conducted with several species of *Daphnia* before concluding whether AMD or LA-PAM effect zooplankton.

# 2.2 Acrylamide (AMD)

As discussed previously, the exposure to AMD monomer is the primary human health risk considered for use of PAM in cosmetics, food processing, and drinking water treatment. This monomer is, therefore, discussed separately from PAM in this report. Data on the chemical and physical characteristics of AMD, as well as data from the available risk literature, are reviewed and summarized in the following sections.

# 2.2.1 Chemical and Physical Properties of AMD

Acrylamide is a solid at room temperature, is highly water soluble with a low potential to partition to organic material including biological lipids, and has a low potential to volatilize from water. It reacts rapidly in free-radical reactions and is susceptible to a variety of reactions (particularly oxidations and hydrolysis) in the environment. Research is underway by the RC to examine the persistence of AMD in the canal environment by quantifying degradation pathways, including exposure to UV light, microbial degradation, and sorption of AMD onto soil. See Table 3 for more data on AMD.

With respect to the production of AMD from the breakdown of LA-PAM, we are unaware of any published experimental data that shows an impact from natural sunlight. PAM gels, when subjected to thermal and irradiation conditions, were found to be stable and did not release AMD under fluorescent light, although Holliman *et al.* (2005) did show that exposure of cross-linked PAM gels to temperatures of 35°C did release AMD at levels that exceeded the 0.1  $\mu$ g/L drinking water standard for the United Kingdom. In aqueous solution at 95 °C, a small amount of AMD was also observed from the unsaturation in a cross-linked gel network (Caulfield *et al.*, 2003b).

International Union of Pure and Applied	
Chemistry (IUPAC) Name:	Acrylamide
Structural formula:	$CH_2 = CH - CONH_2$
Molecular formula:	C <sub>3</sub> H <sub>5</sub> NO
Molecular weight (MW):	71.09
Chemical Abstracts Service (CAS) No.:	79-06-1
European Inventory of Existing Chemical	201-173-7
Substances (EINECS) No.:	
Synonyms:	acrylic acid amide, 2-propenamide, ethylene carboxamide, propenoic acid amide, vinyl amide
Physical state:	White crystalline solid at ntp
Solubility:	640 g/L (25 °C)
Melting point:	84 °C
Vapor pressure:	0.9 Pa at 25 °C for solid AMD
N-octanol-water partition coefficient (K <sub>OW</sub> ):	-1.0
Density	1.127 g/cm <sup>3</sup> at 30 °C

Table 3. Chemical and physical properties of AMD (European Commission, 2002).

## 2.2.2 Human/Animal Health Effects from AMD

The neurotoxic, carcinogenic, and genotoxic effects of industrial exposure to AMD have been studied in humans and laboratory animals. Currently, a European Union-funded project entitled Heat-Generated Food Toxicants (HEATOX) is focusing on the toxic effects of AMD following exposure to heat-induced toxicants from carbohydrate-rich food. These effects include: male reproductive toxicity, tumorigenicity, and neurodevelopmental effects (Hellenäs and Abramsson-Zetterberg, 2005).

## 2.2.2.1 Neurotoxicity

Acrylamide has been shown to induce neurotoxicity in occupationally exposed workers and in cases of acute poisoning. Acrylamide neuropathy represents the classical model of the distal axonopathy of the dying-back type, and chronic AMD intoxication causes a sensory neuropathy (Tandrup and Jakobsen, 2002). Human epidemiological studies have demonstrated a significantly elevated incidence of neurotoxicity in highly exposed populations. Extensive studies in rodents and other laboratory animals have provided evidence that exposure to AMD produces distal swelling and the secondary eventual degeneration of axons in the central and peripheral nervous systems, which is characterized by lack of coordination and skeletal muscle weakness (LoPachin et al., 2002a,b; 2003; LoPachin, 2004). A growing body of evidence now indicates that the nerve terminal is a primary site of AMD action. The damage to the nerve terminal precedes the injury to the axon that is responsible for the autonomic, sensory and motor defects that accompany AMD intoxication in subchronic studies (LoPachin et al., 2002a,b; 2003; LoPachin, 2004). Note that the U.S. EPA reference dose for AMD of 0.0002 mg/kg bw/day (0.2 µg/kg bw/day) was derived from the NOAEL for nerve damage in a drinking water exposure study in rats using a 1,000-fold uncertainty factor (U.S. EPA, 1988). This reference dose will be compared to actual field sample concentrations in Section 4.0, further in this document.

# 2.2.2.2 Carcinogenicity

In animal studies, chronic exposure to AMD has been shown to cause cancer and adverse effects on reproduction and fetal development (Manson et al., 2005). Table 4 lists AMD human cancer classifications by national and international agencies (Manson et al., 2005). Acrylamide has been found to be carcinogenic to experimental mice and rats, causing tumors at multiple organ sites in both species when given in drinking water or by other means (Rice, 2005). The U.S. EPA (1988) lists oral and inhalation carcinogenicity assessment for lifetime exposure. In the case of oral intake, concentrations at 0.8 and 0.008 µg/L could lead to a cancer risk of 1:10,000 and 1:1,000,000, respectively. However, concentrations of AMD measured in LA-PAM-treated canals are below the current U.S. EPA drinking water standard of 0.5  $\mu$ g/L (Code of Federal Regulations [40 CFR §141.111]), and would last for only several hours during application. The potential for long-term accumulation of AMD is discussed below.

	2	
Agency	Classification	Explanation
IARC	2A	Probable human carcinogen
USEPA	B2	Probable human carcinogen
ACGIH	A3	Confirmed animal carcinogen with unknown relevance to
		humans
NTP	n/a	Reasonably anticipated to be a human carcinogen
Notes: IARC	- International Agency	for Research on Cancer

 Table 4.
 Acrylamide cancer classifications.

USEPA – United States Environmental Protection Agency

ACGIH – American Conference of Industrial Hygienists

NTP - National Toxicology Program

In mice, dermal exposures to AMD increased the incidence of alveologenic lung tumors and initiated skin tumors. Acrylamide administered in drinking water to rats consistently induced peritesticular mesotheliomas, thyroid follicular cell tumors, and mammary gland tumors, as well as primary brain tumors when all such tumors were included in data analysis (Rice, 2005). One of the rat bioassays showed increased numbers of adrenal pheochromocytomas, adenomas of pituitary and clitoral glands, papillomas of the oral cavity, and adenocarcinomas of the uterus. In both humans and experimental animals, a significant fraction of ingested AMD was converted metabolically to the chemically reactive and genotoxic epoxide, glycidamide, which may play an important role in the carcinogenicity of AMD (Rice, 2005).

Epidemiologic studies of possible health effects from exposures to AMD have not produced consistent evidence of increased cancer risk in either occupationally exposed workers or the general populations of several countries in which AMD was present in certain foods and beverages (Rice, 2005). A doubling of risk for pancreatic cancer was observed in the most highly exposed workers within the largest industrial cohort, but no consistent exposure-response relationships were identified (Rice, 2005). Retrospective re-analyses of previously conducted case-control studies of cancer incidence in several European populations identified no causal relationship between consumption of foods or beverages that contain AMD and the incidence of cancers at various sites including kidney, large intestine,

bladder, oral cavity, pharynx, larynx, esophagus, breast, and ovary. These retrospective studies of cancer incidence in relation to AMD in food have limited power to detect increased cancer risks, and have been criticized on various grounds (Rice, 2005).

Based on different exposure assessments, different human lifetime cancer risk predictions have been made (Andersen, 2005), varying over three orders of magnitude from 2 x  $10^{-3}$  to  $1.9 \times 10^{-6}$ , with a mean of  $5.0 \times 10^{-4}$ . In the European Union (EU), AMD has been limited to 0.1 ppm for dermal exposure in leave-on cosmetic products and 0.5 ppm for other cosmetic products, as suggested by the EU Scientific Committee on Cosmetic Products and Non-food Products Intended for Consumers (see

http://europa.eu.int/comm/food/fs/sc/sccp/out95\_en.html). An Australian risk assessment suggested negligible health risks from AMD in cosmetics, and a National Toxicology Panel recently concluded that it was appropriate to limit AMD levels to 5 ppm in cosmetic formulations (Andersen, 2005).

Rudén (2004) compared 14 assessments of AMD and cancer risk made by different expert groups during the years 1976 to 2002, in terms of their overall conclusions and their use of primary data. The differences in the overall conclusions were explained to a large extent by an evolving database. The risk assessors agreed considerably on how to interpret and evaluate the available primary data, but the coverage of the available references was low. The arguments used in the public debate to question the expert risk assessments were summarized, and Rudén (2004) argued that the arguments were not based on the principles generally accepted in toxicological risk assessment. Rudén (2004) indicated that when expert risk assessors examined the potential of AMD to cause cancer, a majority (11 assessors of 14) concluded that AMD was carcinogenic in animals and was likely to be carcinogenic in humans (Rudén, 2004).

Sharp (2003) noted that a translation of all the recent AMD data into sensible publichealth advice is proving difficult. The American Council on Science and Health (2002) stated that there is "no credible evidence that acrylamide in foods poses human cancer risk." New Zealand food safety experts, using a NOAEL for AMD of 0.1 mg/kg bw/day, also estimated that people eating fried potatoes are at a very low risk of cancer from this source. European Union experts, on the other hand, stated that the risk from exposure to AMD could not yet be determined. Similarly, the U.S. Food and Drug Administration (FDA), with its public debate on AMD, emphasized what is still not known (Sharp, 2003).

## 2.2.2.3 Reproductive Risks

 An expert panel, convened by the National Toxicology Program and National Institute of Environmental Health Sciences through the Center for the Evaluation of Risks to Human Reproduction, concluded that although there were no human data available on developmental toxicity of AMD, the data were sufficient to conclude that AMD is a reproductive toxicant in male rats and mice bred to untreated females (Manson et al., 2005). The rodent data were assumed to be relevant to humans. LOAELS from some of the relevant studies reviewed by Manson et al. (2005) follow. For this report an uncertainty factor of 1000 was applied to each NOAEL when the data were included in Figure 1 (page 29).

- A NOAEL of 4 to 5 mg/kg bw/day<sup>1</sup> (4,000 to 5,000 µg/kg bw/day) for developmental toxicity based on marginal decreases in pup weights during the postnatal period was identified in rats with maternal drinking water or gavage exposures.
- A NOAEL of 15 mg/kg bw/day (15,000 µg/kg bw/day) for developmental neurotoxicity based on alterations in activity patterns and decreased auditory startle amplitude was identified in rats with maternal gavage exposures. This dose also produced signs of maternal neurotoxicity.
- A NOAEL of 45 mg/kg bw/day (45,000 µg/kg bw/day) for developmental toxicity based on decreased fetal body weight was identified in mice with maternal gavage exposures (Manson *et al.*, 2005).
- A NOAEL of 5 to 8 mg/kg bw/day (5,000 to 8,000 µg/kg bw/day) for male reproductive toxicity in rats was identified with drinking water exposure; toxicity was manifested as impaired delivery of sperm to the female genital tract and reduction of litter size due to increased postimplantation loss.
- A NOAEL of 7 to 14 mg/kg bw/day (7,000 to 14,000 µg/kg bw/day) for male reproductive toxicity in mice was identified with drinking water exposure; toxicity was manifested as a decrease in litter size and increased post implantation loss. The data suggest that AMD has no effect on female reproductive function in rats or mice at these exposure levels (5 to 14 mg/kg bw/day; 5000 to 14,000 µg/kg bw/day). The expert panel found the data to indicate that the male reproductive toxicity of AMD in rodents is reflected in multiple effects, including impairment of mating ability and postimplantation loss at these doses, and at higher doses, alterations in sperm functions (Manson *et al.*, 2005).

The National Toxicology Program's Expert Panel on the Reproductive and Developmental Toxicity of Acrylamide was not able to separate developmental effects of AMD on rat or mouse offspring from effects that could have been due to maternal toxicity at exposure levels of 10 mg/kg/day (10,000  $\mu$ g/kg bw/day). The Panel was also not able to determine whether maternal gestational or lactational exposure, or both, was critical for producing developmental toxicity. There are no human data available on reproductive toxicity of AMD. These data were considered sufficient by the Panel to conclude that AMD is a reproductive toxicant in male rats and mice bred to untreated females and they are relevant to humans (Manson *et al.*, 2005). Acrylamide, tested in a two-generation reproductive animal study at concentrations up to 5 mg/kg bw/day in drinking water, was associated with prenatal lethality at the highest dose, with evidence of parental toxicity (Andersen, 2005). The NOAEL was close to the 0.5 mg/kg bw/day dose.

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<sup>&</sup>lt;sup>1</sup> mg/kg bw/day is milligrams per kilogram of body weight per day

Acrylamide can be absorbed through the skin and has been shown to be a germ-cell clastogen (one that causes breaks in chromosomes) resulting in a genetic risk for exposed chromosome through changes in location for segments of DNA. Translocations occur during DNA replication and cell division. The researchers used two approaches to examine the translocation response differences between dermal and intraperitoneal exposures.

One approach used the dominant-lethal test which is based on fetal survival after exposure of one parent to AMD. Since AMD is a testicular toxicant, male mice were exposed by dermal application of 50 mg/kg AMD per day on five consecutive days or to five daily ip injections of 50 mg/kg AMD (Adler *et al.*, 2004). One day after the end of exposure, the males were mated to untreated females of the same hybrid stock for four days and females were changed every four days for a total of five matings. An increase in dead fetal implants as compared to controls (dominant lethal effects) was found during matings 1 to 3. For ip exposure, the measures of dominant lethal effects were 81.7, 85.7, and 45.4 percent, respectively for the three matings; for dermal exposure the corresponding values were 22.1, 30.6, and 16.5 percent, respectively, demonstrating the role of the dermal barrier in reducing risk.

In the heritable translocation assay, male mice were treated with five dermal exposures of 50 mg/kg AMD and mated 1.5 to 8.5 days after the end of exposure to untreated female mice (Adler *et al.*, 2004). Pregnant females came to term and all offspring were raised to maturity. A total of 475 offspring were screened and 41 translocation carriers were identified. Adler *et al.* (2004) concluded that impacts were weighted more toward dermal exposure (ip/dermal exposure = 0.39). Though these results could be applied to realistic calculations of genetic risk for dermally-exposed workers, the concentration of AMD applied to the mice is more than 10 times above the chronic levels needed to observe health impacts (Manson *et al.*, 2005). As will be shown below, these chronic exposure levels are about three orders of magnitude above any concentrations measured in the field.

# 2.2.2.4 Ecological Risks from Acrylamide

A review of the literature found no reports of ecological toxicity from AMD associated with LA-PAM use. However, one of the uses of AMD is as a grouting agent, where large amounts of AMD are injected into porous systems and allowed to polymerize *in situ* to form a polymer that seals the system. In this case, polymerization is not well controlled and the process can potentially release large amounts of AMD. Although this application is entirely different than use of industrially synthesized PAM, the results of these examples provide information on the ecological toxicity of AMD.

One example of a large volume environmental release of AMD occurred on October 1997, when inhabitants of the Bjare peninsula in southwestern Sweden observed that their cows were suddenly becoming paralyzed and dying, and dead fish were floating in breeding pools (Reynolds, 2002). Concurrently, a railroad tunnel was being bored through the Hallandsås horst, a ridge of porous rock between two seismic faults. Contractors for the national railway agency, who had been working for months to plug water leaks in the tunnel, injected 1,400 tons of the sealant Rhoca-Gil into cracks in the tunnel walls, which contaminated ground and surface water with AMD.

Weideborg *et al.* (2001) investigated the monitoring results and environmental risk caused by releases of nonpolymerized monomers during use of the AMD-based grouting

agent Rhoca-Gil (Siprogel). Drainage water from the tunnel Romeriksporten was monitored with respect to AMD and methylolacrylamide, as leakage of these substances was observed earlier in connection with similar constructions where Rhoca-Gil was used (Weideborg et al., 2001). Concentrations of AMD and methylolacrylamide in the draining water showed that these substances leaked out both in connection with the injection of Rhoca-Gil and in connection with after-injection using other grouting agents. Gel formation studies with Rhoca-Gil showed that a low degree of polymerization, resulting in large leakages of monomers, could be expected if the product was diluted with water. Results from the Weideborg et al. (2001) investigation of the environmental fate of methylolacrylamide showed that this substance was chemically transformed to AMD at the highly alkaline conditions (i.e., pH > 10) of the tunnel. Ecotoxicological testing of the substances and an environmental effects assessment for the receiving water (River Alna and the Oslofjord) suggest that the discharge of AMD and methylolacrylamide may have caused the health effects observed for the aquatic life in the river and in a limited area of the fjord. Weideborg et al. (2001) summarized literature values and reported their experimental results for the effects of AMD on aquatic organisms (Table 5). In contrast to the case of the Rohca-Gil grouting agent, the LA-PAM used in canal sealing is fully polymerized with <0.05% AMD monomer; thus there will be no widespread release of significant amounts of AMD to the environment

Parameter	Value for Acrylamide	Units
Bioconcentration factor	0.85 to 1.55	()
Biodegradability	100	%
Ecotoxicological data, freshwater:		
Fish, 96 h LC <sub>50</sub>	85 to 460	mg/L
Fish, chronic NOAEL <sup>A</sup>	12 to 50	mg/L
Crustacean, 48 h LC <sub>50</sub>	98 to 230	mg/L
Crustacean, chronic NOAEL <sup>B</sup>	2 to 60	mg/L
Algae, 72 h EC <sub>50</sub>	33 to 72	mg/L
Algae, 72 h NOAEL	16	mg/L
Ecotoxicological data, marine:		
Fish, 96 h $LC_{50}$	130 to 400	mg/L
Crustacean, 48 h $LC_{50}^{C}$	72 to 109	mg/L
Crustacean, chronic NOAEL <sup>C</sup>	2 to 5	mg/L
<sup>A</sup> Onchorhynchis mykiss		

Table 5. Ecotoxicological findings for acrylamide (Weideborg et al., 2001).

<sup>B</sup> Daphnia magna

<sup>C</sup> Mysidopsis bahia

Brown *et al.* (1982) dosed a river with AMD, targeting a river water concentration of 50  $\mu$ g/L for six hours, and then 6  $\mu$ g/L for about 43 days (with spikes of 50  $\mu$ g/L every seven days) to simulate long-term release of AMD into rivers. They found a reduction in species diversity of insect fauna after five hours of exposure to AMD at the higher concentration. Within 21 days, only one species was measured in the river, though they noted that some colonization occurred after cessation of AMD dosing. They also reported that AMD was not

adsorbed onto sediments, and did not appear to be degraded in the river environment under the conditions tested.

### 2.2.3 Exposure Assessment

Exposure to AMD is considered to present a potentially significant risk to humans and will be examined here. Because of the low toxicity of PAM, and the general consensus of previous risk assessments that PAM in drinking water does not represent a significant risk to humans, exposure to PAM will be examined only for ecological risk and, briefly, for worker risk during application in canal environments. This section will consider pathways or "modes" of exposure, including inhalation and ingestion pathways.

## 2.2.3.1 Inhalation Pathway

While this risk characterization considers human exposure to AMD through its presence in canal water, it is important to note that most human exposure to AMD is currently from smoking cigarettes along with consuming foods and drinking water that contain AMD. Using literature sources, the Expert Panel on the Reproductive and Developmental Toxicity of Acrylamide presented estimates of human AMD exposure (in units of  $\mu$ g/kg bw/day) by sources and population groups (Manson *et al.*, 2005). The AMD concentrations presented in Table 6 are estimates of background exposures. In many cases, estimates of human exposure to acrylamide are determined from adducts it forms with hemoglobin in red blood cells. Blood samples are collected and analyzed for the presence of adducts.

Sources of Exposure	Mean or Median	90th Percentile or	
	μg/kg bw/day	Upper Boundary	
Diet: general population	0.43	0.92	
2- to 5-year-olds	1.06	2.31	
Drinking water	No data	< 0.01	
Personal care products	~0.5	1.1 (female)	
Cigarette smoking	0.67 (from cigarette data)	1.3	
	2.6 (from adduct data)	~6	
Occupational exposures	1.4 to 18	43 (based on PEL*)	
Totals (adults)			
General population			
Nonsmokers	0.98	2.0	
Smokers	0.85 (from adduct data)	3.2	
	1.7 (from cigarette data)		
	3.6 (from adduct data)		
Occupational exposure		45 to 52	
Nonsmokers	2.4 to 19	45	
Smokers	3.1 to 20 (cigarette data)	46	
	5 to 22 (adduct data)	51	

Table 6. Estimates of human acrylamide exposure from Manson et al. (2005).

\*permissible exposure limit

Among 70 nonsmokers, the AMD-adduct levels varied by a factor of 5, and ranged between 0.02 and 0.1 nmol/g with considerable overlap between different dietary groups (Hagmar *et al.*, 2005). The median hemoglobin (Hb) adduct level in the randomly selected group of nonsmokers (0.031 nmol/g) was compatible with earlier studies (Hagmar *et al.*, 2005). A significant difference was found between men with high dietary exposure to AMD compared to men with low dietary exposure (P = 0.04). No such difference was found for women. A higher level (range: 0.03 to 0.43 nmol/g) of the AMD-Hb, due to AMD in tobacco smoke, was found in smokers (Hagmar *et al.*, 2005). Smoking women with high dietary exposure to AMD had significantly higher AMD-Hb levels compared to smoking women with low dietary exposure (P = 0.01). No such significant difference was found in smoking men (Hagmar *et al.*, 2005).

For inhalation exposure, the large multi-site epidemiology study of chemical workers was essentially negative for a causal association between inhalation exposure to AMD and cancer (Manson *et al.*, 2005). Worker exposure to AMD during application of LA-PAM to irrigation canals can be managed by using personal protective equipment such as dusk masks. Volatilization of AMD from water containing hydrated PAM is negligible.

# 2.2.3.2 Ingestion Pathway

Hagmar *et al.* (2005) studied the variation in dietary exposure to AMD through measurement of Hb adduct levels from AMD, as a measurement of internal dose, in a sample from the blood bank of the Malmö, Sweden, Diet and Cancer Cohort (n = 28,098). The blood donors were well characterized with regard to their food habits, and 142 individuals were selected to obtain the highest possible variation in the adduct levels from AMD (none, random or high intake of coffee, fried potatoes, crackers and snacks, food items estimated to have high levels of AMD). The variation in the average internal dose, measured as Hb adducts, was somewhat smaller than estimated for daily intake by food consumption questionnaires in other studies. Hagmar *et al.* (2005) concluded that the observed relatively narrow interindividual variation in AMD-adduct levels indicated that estimates of individual dietary AMD intake would have to be precise to be useful in future cancer epidemiological studies.

While the Maximum Contaminant Level Goal (MCLG) for AMD concentrations in drinking water is zero, the actual MCL, as determined by the U.S. EPA, is a treatment technology based value. It requires that public drinking systems use certified PAM products. The polymer dose is not to exceed 1 mg/L and have an acrylamide content that is no greater than 0.05%. The restrictions on the polymer and monomer limit the acrylamide concentration in treated waters to no more than 0.5  $\mu$ g/L. The approach used for determining an MCL for drinking water has applicability for LA-PAM use in canals.

The National Sanitation Foundation / American National Standards Institute (NSF/ANSI) Standard 60: Drinking Water Treatment Chemicals – Health Effects is the nationally recognized health effects standard for chemicals that are used to treat drinking water. Use of LA-PAM for treating drinking water requires a NSF/ANSI-Standard 60 certification and unannounced audits. The typical use level for LA-PAM application is limited to a LA-PAM level of 1.0 mg/L and an AMD level of less that or equal to 0.05 percent in the polymer, or equivalent (as listed under the Code of Federal Regulations [40]

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CFR §141.111]) for a carryover of not more than 0.5 ppb of AMD into the finished water. The Safe Drinking Water Act limits for AMD, adopted by the ANSI Standard 60, are listed in Table 7.

Contaminant	MCLG	MCL or	Potential Health Effects from	Sources of
	(mg/L)	11	ingestion of water	Contaminant in
		(mg/L)		Drinking Water
Acrylamide	Zero	0.5 μg/L	Nervous system or blood	Added to water during
		(TT)	problems; increased risk of	sewage/wastewater
			cancer	treatment

Table 7.	Regulatory	limits t	for AMD.
	0 2		

Source: <u>http://www.epa.gov/safewater/mcl.html</u>

Because AMD does not appear to be formed as a transformation product of LA-PAM, the primary human health risk from the use of LA-PAM in canals is from exposure to AMD residues in the LA-PAM polymer. Currently, the AMD concentration in potable LA-PAM products is mandated to be less than 0.05 percent, although it is typically found in lower concentrations. With application protocols designed to limit exposure to AMD to less than 0.05 percent of LA-PAM, the human exposure to AMD from LA-PAM usage as a canal seepage reduction technology will be similar to that considered for an exposure assessment from the use of LA-PAM in drinking water as a coagulant. For appropriate consideration of AMD and LA-PAM exposures when used as a seepage control technology, a general description of LA-PAM application in agriculture is presented below.

The characterization of the risk from AMD via the ingestion pathway requires knowledge of LA-PAM application rates, the flow characteristics of individual canals being treated, and assumptions of LA-PAM hydration and AMD release into the canal waters. These issues are described in detail in Section 3.0. Possible environmental accumulation of AMD is described in Section 4.0.

### 3.0 GENERAL DESCRIPTION OF PAM APPLICATION IN AGRICULTURE AND CANAL SYSTEMS

## 3.1 Introduction

LA-PAM has been used in agriculture for over 10 years to control erosion in furrow irrigation (Lentz *et al.*, 2002) by stabilizing soil structure, thereby increasing infiltration. More recently, LA-PAM has been used in canals to reduce infiltration (and loss) of water. Farm managers have used LA-PAM products in irrigation furrows to improve water quality by reducing sediment load and loss of nutrients. During this application, LA-PAM is applied during the initial advance of water across the field, followed by normal irrigation water with no additional LA-PAM added. Conservation practices for use of LA-PAM in agricultural fields have been described by the U.S. Natural Resources Conservation Service (2001).

The use of LA-PAM as a canal sealant technology has been considered only in the past decade. It is assumed that LA-PAM will be applied intermittently, perhaps one to four times per year, in accordance with the USBR field application guidelines. Field application protocols have not been finalized by USBR, but they currently specify a limit of 10 lbs/ac per treatment, with one to two treatments per year, regardless of the flow rate in the canal.

Applying LA-PAM to the canal lasts on the order of hours, so the elevated concentrations of LA-PAM and AMD in canal water will be transient. From experiments conducted during Water Years 2005 and 2006, LA-PAM and AMD concentrations were shown to dissipate rapidly after application was complete, on the order of hours. Concentration declines were attributed to either dilution from upstream waters or sorption/loss of LA-PAM from the water column after binding (or adsorbing) to suspended sediment and settling to the canal bottom (data from case studies are presented below). For the purposes of this study, only the 30-mole-percent anionic form of LA-PAM is being investigated, because only anionic forms of PAM are being considered for use in canals. Moreover, 30-percent anionic PAM is known to be the most effective anionic content (charge density) for flocculation in many soil-related applications such as furrow erosion control and in canal seepage control applications, based on the LA-PAM products that are generally known to have been used.

During hydration of powdered LA-PAM, the linear PAM molecules become hydrated random coils. These polymers then interact with suspended particles in the water that have been eroded from the canal bed or carried off agricultural fields with surface runoff. These particles (or fines) in the soil bind with the LA-PAM by electrostatic forces, hydrogen and chemical bonding, and by displacing inner solvation-sphere water molecules (Malik and Letey, 1991; Laird, 1997), which may be thermodynamically favored. This process stabilizes soil aggregates, making them less susceptible to erosion in furrow applications, and results in aggregates of particles, called flocs, that are larger and, therefore, more readily settle in a flowing water environment. Dissolved LA-PAM molecules irreversibly bind to suspended sediment and the soil-lined channel, effectively removing the polymer from the stream flow (Lentz *et al.*, 2002). In fact, the analysis of LA-PAM residues in soils is complicated by the strong adsorption of PAM onto soils, primarily with the clay fraction of soils and less strongly with the sand fraction, which has fewer reaction sites. Thus, as PAM encounters suspended soils from the canal bed, it is removed from the flowing water by forming soil/PAM complexes that settle to the bottom of the canal forming a seal.

The degree of interaction depends on both the properties of the polymer and properties of the soil (Seybold, 1994). Important polymer properties are type and amount of charge on the polymer chain (charge density or charge frequency), polymer configuration (linear, deliberately branched, extent of branching), molecular weight, and molecular dimensions. Molecular dimension (random coil length) is determined by the ionic strength (conductivity) of the water, pH, and presence of polyvalent counterions to the charge on the polymer. For anionic PAM in typical irrigation waters, calcium and magnesium are likely to be the most important counterions due to their concentration and polyvalency. The sodium adsorption ratio is a measure of univalent (i.e.,  $Na^+$ ) versus divalent ( $Ca^{2+}$ ,  $Mg^{2+}$ ). Without divalent cations, which act as the binding agent between the particle and the polymer, flocculation will often not occur. The first publications on this effect go back to 1955 (Michaels and Morelos, 1955), but Lu et al. (2002) and Somasundaran et al. (1988) also discuss these relationships. Important soil properties that affect sorption are type and amount of clay, the type and amount of any other particles present in the 1- to 100-micron size range, cation exchange capacity, and the presence of organic dispersants such as humic and fulvic acids. Water temperature is also important due to the decrease in particle settling rates presumably due to the increasing viscosity of water as temperature decreases.

The differences in adsorption of LA-PAM appear to be the result of changes in polymer configuration, which is influenced by the degree of hydrolysis, amount of surface charge, and solution pH. Maximum adsorption of anionic PAM occurs when the polymer is in its most extended configuration, as opposed to being tightly coiled (Seybold, 1994). Anionic PAMs with 20 percent hydrolysis have been reported by Malik and Letey (1991) as the most effective for stabilizing soils, because 20 percent hydrolysis provides the most extended polymer chain configuration for adsorption. Malik and Letey (1991) determined adsorption isotherms for three tritium-labeled PAM compounds with negative charge densities (percentage of acrylic acid monomer) of 40 percent, 21 percent and 2 percent on three soils, differing in clay content and type, and on washed quartz sand of three size fractions. One of the soils was pretreated to create a high exchangeable sodium percentage (ESP) of 34. Results of these experiments showed that adsorption of PAM on sand was only slightly less than on soil, and that adsorption on the high ESP soil was significantly higher than on the untreated soils. Adsorption was approximately the same for all soils of similar aggregate sizes, suggesting that the PAM compounds did not penetrate the aggregates. The investigators concluded that MW and conformation of the polymer affected adsorption, with increasing MW and increasing chain extension leading to increasing adsorption. Thus, the literature shows that PAM binds tightly to soils and, as discussed above, is removed from flowing water. Acrylamide, alternatively, has very high water solubility (i.e., 640 g/L), does not bind to soils, and is carried with flowing water. The lack of absorption of AMD thus has potential implications for water that leaves the canal and flows into receiving water bodies.

# 3.2 Application Methods for LA-PAM in Water Delivery Canal Systems

Generally, PAM used for reducing seepage in water delivery canal systems is typically applied using five possible procedures: 1) dry powder in dry canals, 2) dry powder added to flowing canal water, 3) partially hydrated dry powder in a dry canal, 4) emulsion- or dispersion-form PAM in a dry canal, or 5) partially hydrated-emulsion- or dispersion-form PAM in a dry canal. The most common method is adding dry powder to flowing canal water (Scenario 1, below). It is commonly added at a rate equivalent to a surface treatment of 5 to 10 lbs/ac. When dry LA-PAM is added to flowing canal water, the polymer uncoils and hydrates at a rate that is not fully understood, but appears to depend on water temperature, water chemistry, and stream turbulence. As the polymer dissolves, residual AMD is potentially released.

Besides the five typically used PAM application methods stated above, PAM can be applied to canals by: 6) partially hydrated dry PAM added to flowing canal water, 7) emulsion- or dispersion-form PAM added to flowing canal water, and 8) partially hydrated emulsion- or dispersion-form PAM added to flowing canal water. The principal reason that these last three methods have not been used is that USBR application guidelines permit only use of dry LA-PAM. In any case, the lack of reliable truck-mounted PAM hydration and spray equipment and the logistics of making clean water available for PAM hydration in remote locations will render emulsion- or dispersion-form PAM more difficult to apply. In the future, the improvement in the application methods could increase the use of prehydrated LA-PAM. If these or other application techniques were to become commercially viable then the comparative risk of these techniques would need to be evaluated.

• **Scenario 1.** *Addition of dry, powdered LA-PAM to a dry canal.* Dry, powdered LA-PAM is typically applied to the bottom and sidewalls of a dry canal (i.e., at the

beginning of the irrigation season) at discrete (e.g., 10-foot) intervals. Linear anionic polyacrylamide then becomes hydrated when water is introduced into the water delivery canal. In this scenario, AMD would be released into the water column and potentially carried into the soil by infiltrating water. The amount of AMD carried into the soil depends on the ratio of water carried down the canal to the amount of water infiltrating into the soil. The highest concentrations are expected to occur when water first enters the canal, when the initial pulse of water, called the leading edge, may entrain nonhydrated and partially hydrated LA-PAM granules as they travel downstream. Therefore, the leading edge could have elevated concentrations of LA-PAM and AMD; field studies are ongoing to examine this potential. The water velocity of the leading edge is typically low because water managers tend to slowly charge the canals at the beginning of the water season, and because the bulk of this early season water infiltrates into dry canal sediments. The AMD released from dissolving LA-PAM is concentrated in a fraction of the entire canal flow. The concentration of AMD moving into the soil and potentially toward ground water is expected to be highest for this scenario.

- Scenario 2. Addition of dry, powdered LA-PAM to flowing water. In this scenario, LA-PAM is added to the canal water, starting at the lower end of the application reach and moving upstream. After PAM hydrates, it attaches to suspended sediment, and then settles with soil floccules. The AMD released from dissolving LA-PAM is diluted in the entire canal flow; thus, the resulting AMD concentration is substantially lower than in Scenario 1. All AMD released remains in soluble form in the canal water, though a small amount seeps into canal sediments with infiltrating water. Because this scenario requires that the canal is already charged, any early season infiltration into canal banks has already occurred. Therefore, the perimeter of the canal is already saturated and the seepage loss will consequently be reduced compared to initially dry canal conditions.
- Scenario 3. Addition of partially hydrated LA-PAM to a dry canal continuously over the treatment reach. Partially hydrated LA-PAM, formed by carefully mixing dry, powdered LA-PAM and water, is typically sprayed through a pressurized nozzle. Once applied, the partially hydrated LA-PAM solution is pulled into the dry canal sediments by the soil matric potential, where it can react with the canal sediments prior to water entering the canal. Therefore, mechanisms of seepage reduction for liquid applications will likely differ from those discussed for dry, powdered LA-PAM. Relative to a given application rate of granular LA-PAM, this method results in the relatively uniform distribution of a lower concentration of LA-PAM over the application reach. The application of partially hydrated LA-PAM can be used to target specific areas of the canal (e.g., side or bottom), and can be applied above the typical high water line to help prevent erosion. Acrylamide release rates would presumably be slightly higher because the LA-PAM is already partially hydrated and thus the AMD would be mobile more quickly. This method is more time consuming and requires a source of water and specialized equipment to mix the partially hydrated LA-PAM solution to the proper consistency.
- Scenarios 4 and 5. Addition of emulsion- or dispersion-form PAM to a dry canal. The use of emulsion- or dispersion-form PAM products as a canal sealant option

provides the benefits of a wet on dry application without the potential logistical issues of dealing with a partially hydrated PAM solution (discussed in Scenario 3). Stored emulsions, however, must be protected from repeated freezing, need to be mixed properly prior to use, and result in the need to dispose of drums. Emulsions or dispersions are typically fed from their container into a spray nozzle, where they may be diluted with water prior to being sprayed onto a dry canal. Acrylamide release rates to the environment would likely be similar to those described in Scenario 3, but this is somewhat conjectural given that emulsions and dispersion forms of PAM have not been considered for use in canals and the RC has not examined their behavior.

# 3.3 Expected Concentrations of LA-PAM and AMD in Canal Waters

Because of the relatively new usage of LA-PAM in canals, data on LA-PAM and AMD concentrations in canal waters are unavailable. To date, we are unaware of any research findings in the peer-reviewed literature that describe LA-PAM application for seepage control in canals, the seepage reduction efficiency, or the downstream concentrations of LA-PAM and AMD. During Water Years 2005 and 2006, field tests were conducted at several sites in Colorado, each with full-scale canal systems that will provide "real world" tests of LA-PAM. The field tests focused on the application of dry LA-PAM in a flowing canal (Scenario 2).

At each of these test sites, canal reaches were measured for flow rate, wetted perimeter and other geometric characteristics that could be used to estimate water discharge rates. In some cases, the flow rates were measured directly. Table 8 provides geometric and flow data for four sites in western Colorado. These sites differ most notably by wetted perimeter, discharge, and water flow velocities. In the case of the Grand Valley Irrigation Company (GVIC) canal, geometries were not obtained. Data for this table were obtained using the following methods:

- Average water velocity: The average velocity was measured 6/10 of the depth (from canal bottom) at equal-spaced points along a perpendicular cross section. Measurements were taken using either an impellor or electromagnetic induction velocity meter.
- Average water depth: The average height of water is measured at equal-spaced points along a perpendicular cross section, or as it passed through a known control structure (e.g., H-flume).
- Discharge: The total volume of water flowing past a perpendicular cross section per unit of time was measured by using individual water velocity measurements and depth measurements, or by the depth of water as it passed through a known control structure (e.g., H-flume).
- Average wetted perimeter: The length of contact along a perpendicular cross section between the water stream and its channel was measured during field studies. The wetted perimeter will vary with the depth of water.

The bottom portion of Table 8 lists the LA-PAM application information for three field application tests conducted in Water Year 2005, including the maximum downstream LA-PAM concentration at two sites (LA-PAM concentrations for Smith Ditch #7 test are not available from the water quality laboratory, though samples were taken). Each test was

conducted with concentrations at 10 lbs/ac, conforming to the draft field application protocols being developed by USBR and the Research Consortium.

						GVIC	
			Kannah		GVIC	Near	Redlands
		Minnesota	Creek	Smith	Below	GVIC	Irrigation
	Units	Ditch	Ditch #2	Ditch #7	Headgate	Office	Canal
Average Seasonal Disch	arge (at h	nead gate)					
Early season (free	cfs	32	15	7	680	300	
water)							
Regular season	cfs	20	10	5	680	300	25
Late season	cfs		5	2.5	680	300	25
		<b>T</b> 1					
		Typical	Ditch Inform	ation			
Wetted perimeter	ft	8.46	6.05	11.1	69	45	14.5
Avg depth	ft	0.93	1.03				
Discharge	cfs	19	6.6	2.8			
Avg velocity	ft/s	3.1	1.3				
LA-I	PAM Apr	olication Info	rmation (use	d in calculat	tions below)		
Application equivalent	lbs/ac	10	10	10			
Length of application	mi	2	1.5	0.8			
Total application time	hr:min	2:30	2:15	3:03			
maximum LA-PAM	ppm	9	16	n/a			
concentration							

Table 8.	Typical characteristics of several ditches and canals in the Grand Valley Area of Colorado
	and information on LA-PAM application rates.

Using known canal geometries, water flow characteristics, and LA-PAM application rates, it is possible to estimate or predict the concentrations of LA-PAM and AMD in the water column downstream of the point of application. Assuming that a sufficient number of field tests were conducted and that laboratory data were available, the predictions could be checked against known concentrations, thus lending some weight behind the assumptions of LA-PAM hydration period and AMD release rates, neither of which is known with certainty, The RC is examining both assumptions. Concentrations of AMD in the canal water were thus calculated based on the known amount of LA-PAM added to the canals under different flow scenarios (Tables 8 and 9). Several assumptions were made for these calculations:

- AMD concentration in the LA-PAM molecule is 0.05 percent of the LA-PAM, which is the upper limit mandated by NSF as part of the NSF/ANSI Standard 60 formulation (e.g., potable grade PAM)
- The LA-PAM mass released into the canal is 28 g for each point application, which is the measured amount applied in the field at individual points along the canal
- LA-PAM dissolution is instantaneous
- AMD release rate is instantaneous, or at the same rate as the polymer dissolution rate

Date	Discharge (cfs)	Stage (ft)	Wetted Perimeter (ft)
5/22/05	13.9	2.17	8.2
8/6/05	1.8	0.87	5.4
7/12/05	5.6	1.46	6.5

Table 9.Relationship of wetted perimeter and discharge near the mid-flume site on Kannah Creek<br/>Ditch #2.

Table 10 lists the known flow characteristics the three canals used for the Water Year 2005 field tests: Minnesota Ditch (MD), Kannah Creek Ditch #2 (KC), and Smith Ditch #7 (SD). Two situations were used to calculate the LA-PAM and AMD concentrations. Situation 1 assumes that the LA-PAM powder will hydrate and mix only in the top 1 inch (2.54 cm) of the water in the canal; this scenario assumes incomplete mixing of the LA-PAM in the canal. Situation 2 assumes complete mixing of LA-PAM in the canal. Each test assumes an applicator fetch of 3 ft (i.e., downstream length of application area), which is a function of the field equipment used to apply the LA-PAM. Column 7 lists the LA-PAM thickness, depending on the scenario; in the case of MD Scenario 2, 0.92 ft is the uniform depth of water across the canal. In other cases where the bottom of the canal was irregular (KC and SD canals), the canal flow area (column 8) was calculated based on channel surveys conducted in the field. The product of columns 5, 6, and 7 (or columns 5 and 7, depending on the test case) is the volume of water (column 9) into which the LA-PAM and AMD are dissolved. Therefore, the volume of water (column 9) divided by the mass of LA-PAM released into the canal at each point, measured in the field at 28 g, is the concentration of LA-PAM in the canal water (column 10). For example, considering MD Situation 1, the calculation would be:

Situation 1 – LA-PAM completely and instantly dissolves in top 1-inch of canal water

(Canal Width)(Applicator Fetch)(LA-PAM layer thickness) = Channel Volume

 $(6.6 \text{ ft})(3 \text{ ft})(0.08 \text{ ft}) = 1.6 \text{ ft}^3 = 44.9 \text{ L}$ 

(LA-PAM mass) / (Channel Volume) = LA-PAM Concentration

(28 g)(1,000 mg/g)/(44.854 L) = 624 mg/L LA-PAM

If the LA-PAM was assumed to fully mix within the entire water column in the canal, the calculation would be:

Situation 2 – Polymer completely and instantly dissolves in the entire application zone volume of treated canal water

(Canal Width)(Applicator Fetch)(LA-PAM layer thickness) = Channel Volume

 $(6.6 \text{ ft})(3 \text{ ft})(0.92 \text{ ft}) = 18.22 \text{ ft}^3 = 515.93 \text{ L}$ 

(LA-PAM mass) / (Channel Volume) = LA-PAM Concentration

(28 g)(1,000 mg/g)/(515.93 L) = 54.27 mg/L LA-PAM

Location	Situation	Q (cfs)	Water Velocity (ft/s)	Canal Width (ft)	Applicator Fetch (ft)	LA-PAM Layer Thickness (ft)	Cross- Sectional Area (ft <sup>2</sup> )	Channel Volume (ft <sup>3</sup> )	Calculated LA-PAM Concentration (µg/L)	Calculated AMD Concentration (µg/L)
MD	1	19.0	3.13	6.6	3	0.08		1.6	624,000	312.0
MD	2	19.0	3.13	6.6	3	0.92		18.2	54,000	27.0
KC	1	4.3	1.12	5.9	3	0.08		1.4	698,000	349.0
KC	2	4.3	1.12	5.9	3		3.86	11.6	86,000	43.0
SD	1	2.8	0.28	10.4	3	0.08		2.5	396,000	198.0
SD	2	2.8	0.28	10.4	3		10.1	30.3	33,000	16.5

Table 10. Calculated concentration of LA-PAM and AMD at a single application point, assuming immediate LA-PAM dissolution and AMD release. Locations are at Minnesota Ditch (MD), Kannah Creek Ditch #2 (KC), and Smith Ditch #7 (SD).

Likewise, the calculation of the AMD concentration in the water column would be identical, except that the AMD concentration in the PAM molecule is 0.05 percent. Therefore, multiplying PAM concentration by 0.05 percent, or 0.0005, yields the AMD concentration shown in Table 10, column 11. The results show that LA-PAM concentrations were estimated to be in the range of approximately 30 to 700 mg/L and the concentrations of AMD were estimated to be in the range 16.5 to 349  $\mu$ g/L (Table 10), depending on the characteristics of the canal. These values are above the U.S. EPA drinking water standard; however, concentrations of LA-PAM above 90 mg/L and AMD above 100  $\mu$ g/L were based on field conditions that assume instantaneous dissolution of LA-PAM and release of AMD, and incomplete mixing of LA-PAM in the water column. When complete mixing is assumed, the concentrations were much lower (see Situation 2 for the examples shown in Table 10).

Table 11 shows the predicted LA-PAM and AMD concentrations, assuming that LA-PAM is applied over the entire application zone. It is clear that the application zone is substantial, with surface areas to be treated exceeding 4,000 m<sup>2</sup> in each case. The calculations performed for these predictions are similar to those described above and they support the predictions in Table 10. For the cases listed in Table 11, the concentrations assume that the canal water is not flowing. Therefore, the LA-PAM and AMD are fully dissolved throughout the water column, and the water column is not being flushed by untreated water. This extremely conservative assumption serves to maximize the concentrations of LA-PAM and AMD in the water. In reality, new water will flow into the treated canal section, thereby diluting any AMD that is released into the water column (the mass of LA-PAM that settles to the bottom of the canal as an LA-PAM/soil floc is no longer included in the calculation of concentration).

Observed LA-PAM concentrations measured in the water below the point of application were typically in the range of 2 to 16 mg/L. These concentrations are similar to the application concentrations estimated for the entire application zone, assuming instantaneous application and dissolution. Concentrations of AMD with these assumptions ranged from approximately 0.8 to 4.0  $\mu$ g/L.

A limited amount of AMD data are available for the studies completed during water Years 2005 and 2006 in canal water in Colorado (Table 12). The samples were collected downstream of the point of application, often immediately at downstream extent of application. The LA-PAM application rates were typical, as shown in Table 8. The sample results show that no concentrations of AMD exceeded the EPA drinking water standard. The samples were not collected to represent either the highest or lowest concentrations that could be expected in the canal, but they do represent real data when granular (dry) PAM was added to flowing water (Situation 2). These samples are part of the continuing work to determine release of AMD from LA-PAM applications.

While predicted concentrations will need to be verified by continuing experiments and actual measurements, they do provide a range of expected concentrations of AMD in the water column. Thus, for a fully mixed canal with an application rate of 10 lbs/acre of canal coverage, the AMD concentrations are predicted to be less than 10  $\mu$ g/L, assuming instantaneous release and no dilution from upstream water sources; both assumptions are very conservative. Other ingestion pathways, primarily through consumption of groundwater adjacent to the treated canal, need to be investigated through field work and predictive modeling.

Site	Estimated Quantity of LA- PAM Applied (g)	Typical Surface Width in Application Zone (ft)	Surface Area of Application $(m^2)$	Typical Cross Sectional Area in Application Zone $(ft^2)$	Typical Wetted Perimeter at High Flow (ft)	Typical Wetted Perimeter at Time of Application (ft)	Wetted Area in Application Zone $(m^2)$	Actual LA-PAM Applied Per Wetted Perimeter (lb/ac)	Static Volume of Water in Application Section $(m^3)$	Calculated Static LA- PAM Application Conc. (µg/L)	Calculated Static AMD Application Conc. (µg/L)
MD	9,947	6.6	6,474	19.8	9	8.46	8,298	10.7	5,926	1,680	0.84
KC	6,767	5.9	4,340	3.9	8.2	6.5	4,782	12.6	865	7,820	3.91
SD	5,579	10.4	4,437	10.1	NA	11.1	4,736	10.5	1,315	4,240	2.12

Table 11. Theoretical application	ation concentration of LA-PAM and AMI	O over the entire application zone.	Assumes that all LA-PAM was added
and dissolved insta	antaneously within the entire application s	section of canal.	

	AMD		AMD		AMD
Sample	Concentration	Sample	Concentration	Sample	Concentration
	µg/L		µg/L		μg/L
MD-646	< 0.1	KC-1276	< 0.1	SD-2413	0.234
MD-651	< 0.1	KC-1277	< 0.1	SD-2414	0.175
MD-660	0.100	KC-1278	0.196	SD-2415	0.207
MD-669	< 0.1	KC-1280	0.205	SD-2416	0.236
MD-678	< 0.1			SD-2418	< 0.1
MD-685	< 0.1			SD-2420	< 0.1
GVIC-2975	< 0.1	Lamar-3006	0.3	Lamar-3141	0.300
GVIC-2976	< 0.1	Lamar-3012	ND	Lamar-3142	0.658
GVIC-2979	< 0.1	Lamar-3015	0.661		
GVIC-2981	< 0.1	Lamar-3024	0.446		
GVIC-2985	< 0.1	Lamar-3026	ND		
GVIC-2988	0.409	Lamar-3027	0.373		
GVIC-2989	0.285	Lamar-3034	<0.1		

Table 12. AMD concentrations determined following application of LA-PAM to Minnesota Ditch<br/>(MD), Kannah Creek, Ditch #2 (KC), and Smith Ditch #7 (SD), Grand Valley Irrigation<br/>Company (GVIC) and Lamar canals,

# 4.0 **DISCUSSIONS**

To examine the risk associated with AMD levels in water as a result of PAM application to canals, the concentrations measured in the field were compared to regulatory levels of acrylamide in drinking water, U.S. EPA risk values, and risk estimates derived from selected studies of AMD toxicity, particularly those related to reproductive effects in animals. This comparison is shown in Figure 1. When preparing Figure 1, all of the acrylamide dose data from the animal studies was divided by a 1000-fold uncertainty factor (equivalent to the UF used in the U.S. EPA oral, noncancer assessment of acrylamide). The adjusted dose was then converted into a drinking water equivalent concentration using the following equation:

Drinking Water Equivalent concentration = Dose ( $\mu$ g/kg bw/day) x body mass (75 kg) x drinking water intake (2L/day).

The drinking water intake assumption is that used by the U.S. EPA and is approximately the 90th percentile intake of tap water from all sources (including that used for reconstitution of beverages, coffee, tea, etc.) from the most recent U.S. Department of Agriculture Continuing Survey of Food Intake by Individuals (U.S. EPA, 2004). The body weight estimate was chosen by the authors of this report, and is close to the 76 kg average body weight for males in the third National Health and Nutrition Examination Survey (IOM, 1997).

Analytical results of samples collected in operational canals during controlled field experiments indicate that observed acrylamide concentrations were 50 percent below drinking water standards, approximately three orders of magnitude below the UF-adjusted

lowest daily doses that caused reproductive impacts in laboratory animals, and about onefourth of the drinking water concentration associated with a one-in-ten thousand lifetime risk for cancer, if consumed over a lifetime (U.S. EPA, 1988). It is about one-thirtieth of the Drinking Water Equivalent Level (DWEL) concentration of  $7\mu g/L$  (U.S. EPA, 2004) calculated from the Reference Dose (RfD) that is protective for the neurotoxicity over a lifetime. Each of the exposure scenarios shown in Figure 1 assumes daily doses throughout a person's lifetime. As described above, AMD presence in canals is short-lived, on the order of several hours per treatment, with one to four treatments per year. Therefore, the assumption of chronic exposures as illustrated in Figure 1 is a conservative estimate of risk.

With respect to exposure through groundwater, given that maximum concentrations of AMD are predicted to be slightly elevated for time periods on the order of hours, and that measured AMD concentrations in canal water were always less than 0.5  $\mu$ g/L, the exposure of humans to AMD through groundwater, if it occurred at all, should be below the drinking water standard, though this possibility should continue to be examined through field experiments and predictive models.



Figure 1. Comparison between AMD concentrations that are known to cause health effects, EPA drinking water standards, and field data collected under this research program. Note that the lines for "RfD concentration" (0.75 μg/L) and "1 in 10000 cancer risk" (0.8 μg/L) almost overlie each other and may be obscured.

#### Contexts do not reflect the views of this agency.

Notes:

- All values presented, except "Field data," were originally presented from laboratory animals studies, and then applied to humans using a 10<sup>3</sup> uncertainty factor suggested by U.S. EPA (1988).
- Data for "Reproductive impacts" taken from Manson *et al.* (2005), and by U.S. EPA (1988), as reported by Smith *et al.* (1986).
- "RfD concentration" calculated based on RfD of 2E-4 mg/kg/day exposure (U.S. EPA (1988).
- Accuracy of data and experimental conditions for referenced studies (i.e., those not conducted in this study) were **<u>not</u>** checked as part of this risk characterization.
- Exposure calculations assume a person of 75 kg weight ingests 2 L/day of water.
- Acute AMD concentrations made with the following calculations:

exposure ( $\mu g/kg bw/day$ )\*(body mass [75 kg])/(liquid consumption [2L/day]) = conc ( $\mu g/L$ ).

Due to the high water solubility of AMD, and its fairly rapid biodegradation, the potential for accumulation of AMD in any specific environmental or biological compartment is effectively nil. Moreover, because LA-PAM has not been shown to degrade to AMD under environmental conditions, the only AMD that will be released during LA-PAM use is as the residual monomer. These concentrations are very low (<0.05 percent of LA-PAM), and will be almost completely retained in the aqueous phase where AMD will undergo biodegradation with a half-life of between 5 and 20 days, depending on temperature and other environmental conditions (European Commission, 2002). While less important, AMD is also susceptible to photooxidative and other free-radical degradation processes. Nonetheless, the RC has undertaken an experimental program to specifically examine degradation of AMD through photooxidation, chemical sorption onto soil, and biodegradation pathways. The results will be incorporated into a final risk characterization report to be completed at the conclusion of this research program.

With respect to the accumulation of LA-PAM in the environment, several environmental processes, including microbial, photochemical, and hydrolytic, will cleave LA-PAM into smaller molecules and hydrolyze the amides on the polymer to carboxylic acids. Linear anionic polyacrylamide is also susceptible to mechanical cleavage (Caulfield *et al.*, 2003a). Preliminary studies conducted by the RC have demonstrated that photochemical oxidization of LA-PAM reduces molecule size. Thus, the conversion products are, similar to LA-PAM, effectively nontoxic and have low mobility. To date, the RC is unaware of any studies that demonstrate environmental accumulation of PAM after repeated applications, even in furrow irrigation applications, where PAM has been used for more than 10 years. However, two studies have reported loss rates of PAM in the environment. Azzam *et al.* (1983) estimated a 10% degradation rate per year, and Cook et al. (1997) reported that 8% of a cross-linked gel degraded in 100 days time (or about 30% year). Though these studies were conducted under different environmental conditions than LA-PAM use in canals, they can be used here as initial estimates of LA-PAM accumulation potential. Thus, if we assume a range of degradation rates, and a 20 lbs/ac application rate per year for 25 years, Figure 2

shows that PAM accumulation becomes asymptotic, reaching a stable LA-PAM mass (in units of lbs/ac) remaining in the canal. The equation used to estimate the PAM mass remaining in the canal is

 $[LA-PAM mass]_t = [Annual LA-PAM applied]_t + ([LA-PAM mass_{(t-1)}]*[Annual loss rate])$ 

where subscripts t and t-1 are current year and previous year, respectively, and units for mass are in lbs/ac. The time to reach stability thus depends on the annual LA-PAM and degradation rates. Additionally, LA-PAM bound to soil is not readily released and is retained on the soil particles as they deposit on the bottom of the irrigation canal, or are removed from the canal as the canal is maintained. Except in cases of catastrophic release (accidents), the concentration of LA-PAM on the soils should remain sufficiently low and immobile. The graph also shows the long term concentration of LA-PAM assuming a one-year half life (Woodrow and Miller (2007) indicate a 45-day half-life of LA-PAM in water). The figure shows a long-term concentration of LA-PAM mass would reach 30 lbs/ca). Further work on this subject is being conducted by the RC to better identify the breakdown mechanisms of LA-PAM.



Figure 2. Environmental accumulation of LA-PAM given a yearly application of 20 lbs/ac and four different annual degradation rates.

Andersen (2005) reported no health effects in animals consuming 464 mg/kg bw/day. We can use this value to estimate the potential health impacts to a child who eats surficial soil containing PAM. Here, we assume that a 10-kg child is exposed to soil containing PAM, and that the child consumes 100 mg soil per day (U.S. EPA, 1996). The long-term concentration levels of PAM in soil are equivalent to 210, 112, 75 and 45 kg/hectare for loss rates of 10%, 20%, 30% and 50% per year, respectively (see Figure 2). Assuming that 10-kg child consumes a 1-cm thick soil layer, ingestion of PAM would be equivalent to 14, 7.5, 5.0, and 3.0  $\mu$ g/kg bw/day for these four loss rates, respectively. Remaining consistent with the uncertainty factor used elsewhere in this document, we divided the 464 mg/kg bw/day value reported by Andersen (2005) by 10<sup>3</sup>, yielding 464  $\mu$ g/kg bw/day. The exposure rates calculated above are still significantly above the adjusted value reported by Andersen (2005).

# 5.0 CONCLUSIONS

This document presents an initial risk characterization of LA-PAM usage in water delivery canal systems. This characterization is based on information obtained, to date, from field experiments and laboratory analyses of water samples collected immediately after LA-PAM application. Though a complete risk assessment of LA-PAM usage is not possible at the present time because of a general lack of concentration and exposure data, the current understanding does allow certain conclusions to be put forth.

Based on the knowledge gained from field experimentation, and provided that the risk management application protocols developed by the RC are used, the following conclusions can be made:

- 1. The concentrations of LA-PAM and AMD are likely to be at, or below, the drinking water standards for time periods on the order of hours, immediately after LA-PAM treatment.
- 2. Elevated concentrations of LA-PAM and AMD are expected in surface water samples immediately after LA-PAM addition to a canal, and in close proximity to the locus of addition. These elevated concentrations will be transient and last for no more than the application time (<1 to 4 hours) in a specific reach of a canal under treatment, and for between 1 to 4 times/year.
- 3. The highest concentrations of AMD expected (based on limited field data) are nearly two orders below the NOAEL for human receptor surrogates. Consequently, little effect is expected for AMD, from an ecotoxicological perspective.
- 4. The highest LA-PAM concentrations expected will be in canal sediments. For biologically sensitive canal systems, care should be taken with LA-PAM applications.
- 5. Depending on the assumptions used in calculations, the predicted concentrations of AMD in canal water will be very low -- close to the drinking water standard  $(0.5 \ \mu g/L)$ . To date, however, field samples collected have contained AMD at concentrations consistently lower than the predicted concentrations. Human exposure of AMD from ingestion of canal water is low, and exposure from potential groundwater contamination would be progressively less. Even if AMD could reach groundwater systems from the transient pulse of AMD in the canal, concentrations of AMD would be lower than levels observed in canal water. Acrylamide would also be diluted in groundwater as it moves, further reducing the concentrations.

- 6. Additional information on the environmental fate of AMD and LA-PAM is necessary for a comprehensive risk assessment of the use of LA-PAM for seepage control, especially as it relates to degradation pathways for AMD in the ambient and groundwater environment.
- 7. Though the findings by Manson *et al.* (2005) (see Sections 2.2.2.2 and 2.2.2.3) have significant bearing on the use of LA-PAM in canals, the exposure analysis conducted in this report indicates that acute AMD concentrations in canal waters will be orders of magnitude below the chronic levels needed to impact human health.

The U.S.EPA is presently preparing an updated health risk assessment for acrylamide as part of the Agency Integrated Risk Information System (IRIS) program. The existing IRIS assessment was completed in 1988. Since that time a number of new studies of the cancer and noncancer health risks associated with exposure to AMD have been published. These studies will be included in the new IRIS Toxicological Review for Acrylamide. Agency estimates that the updated assessment will be peer reviewed in December of 2007 (http://cfpub.epa.gov/iristrac/index.cfm); it will be made publicly available prior to the peer review.

# 6.0 **REFERENCE MATERIALS AND CITATIONS**

Notes: In addition to the references cited in this report, other resources are available, including:

(1) An extensive library of articles dealing with PAM and AMD health impacts, risk assessments, and chemical fate and transport are stored on the DRI website that hosts collaboration projects for the DRI. That website is as follows: http://sakai.dri.edu:8080/portal

(2) The Agricultural Research Service, Northwest Irrigation and Soils Research Laboratory (ARS-NWISRL) maintains a PAM research program and PAM bibliography at their website - http://sand.nwisrl.ars.usda.gov/pampub.shtml.

(3) A second ARS site also contains a bibliography with abstracts at the National Agricultural Library's Water Quality Information Center website: http://www.nal.usda.gov/wqic/Bibliographies/eb9614.html.

(4) The International Programme on Chemical Safety (IPCS) has information on AMD at its website: http://www.inchem.org/documents/pims/chemical/pim652.htm

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## **APPENDIX – TIME LINE AND INFORMATION CONCERNING PEER REVIEW OF THIS DOCUMENT**

This document has undergone several revisions and reviews. The reviewers include members of the Research Consortium (RC), an external panel of experts on toxicology, aquatic ecology, and soil physics, and an internal group of scientists and engineers inside the USBR. The peer review panel (PRP) was organized specifically to provide guidance on the research conducted by the RC and to provide feedback on the risk characterization work.

Date	Activity
Summer/Fall 2005	Development of report outline, literature survey.
October 2005	Convening of PRP in Reno, NV. Discussion of ecological and human
	risk issues of PAM and AMD. Discussion and revision of report
	outline.
November 2005	Circulation of revised report outline.
December 2005	Completion of PAM/AMD bibliography and distribution of literature
	database to panel and research members.
December 20, 2005	Completion of first draft of risk characterization report.
January 2006	PRP completes comments on first draft of risk characterization report.
February 3/4, 2006	Second convening of PRP in Las Vegas, NV. Discussion of current
	status of report, research direction, and research findings.
February 27, 2006	Completion of second draft of risk characterization report and
	distribution for review.
March 29, 2006	RC received comments from USBR review.
April 28, 2006	Completion of third draft of risk characterization report. Distributed to
	USBR and to PRP (May 8, 2006).
May 31, 2006	Received comments from PRP on third draft of report.
June, 2006	Revision of risk characterization report based on comments from PRP
	and internal USBR review.
August 8, 2006	Received additional comments from Dr. Joyce Donohue on fourth
	draft of report, and comments were incorporated into revised
	document.
August 28, 2006	Risk characterization report submitted to USBR as an interim final
	version. Report was distributed to internal and external reviewers for
	additional comments.
December 26, 2006	Received additional comments from USBR, and document underwent
	revision. New data collected from experiments conducted in Water
	Year 2006 added to the report.
February 5, 2007	Risk characterization report presented to the USBR and the PRP as a
	tinal version

The time line for development and review of this document follows:

Members of the PAM Peer Review Panel, and their areas of expertise, include:

Frank Mangravite, Ph.D. Public Works Management, Inc. 35 Jane Way Place, Morris Plains, NJ 07950 Phone: 973-984-6828 fmh2o@aol.com

Expertise: Water treatment systems and the use of a variety of products to improve water quality. Identified by AWWARF as an expert on PAM use and potential risks.

Joyce M. Donohue, Ph.D. Office of Water, Office of Science and Technology Health and Ecological Criteria Division, U.S. Environmental Protection Agency Mail Code 4304T 1200 Pennsylvania Avenue NW, Washington, DC 20460 Phone: 202-566-1098 Donohue.joyce@epamail.epa.gov

Expertise: Worked on the toxicology and risk assessment of PAM in drinking water supplies, and has direct and extensive knowledge of how these risk assessments were developed.

James N. Seiber, Ph.D., Director Western Regional Research Center, USDA, Agricultural Research Service 800 Buchanan Street, Albany CA 94710 Phone: 510.559.5600 /01 jseiber@pw.usda.gov

Expertise: Environmental chemist with expertise in risk assessment. Has served on several National Academy panels on risk of environmental chemicals. Current Editor of the Journal of Agricultural and Food Chemistry, with interest in the risk assessment of AMD in foods.

Dave Herbst, Ph.D. Sierra Nevada Aquatic Research Laboratory University of California Route 1, Box 198, Mammoth Lakes, CA 93546 Phone: 760-935-4536 herbst@lifesci.ucsb.edu

Expertise: Aquatic ecologist with expertise in stream habitat assessment, bioassessment of contaminants, and arid lands streams. Dr. Herbst is well-known in the area of stream ecology and has worked extensively on effects of habitat and contaminant alteration from acid drainage sites.

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Final PAM/AMD Risk Characterization – February 2007

Rodrick (Rick) D. Lentz, Ph.D. Northwest Irrigation and Soils Research Laboratory U.S. Department of Agriculture, Agricultural Research Service 3793 N. 3600 E. Kimberly, ID 83341-5076 phone: 208-423-6531 lentz@nwisrl.ars.usda.gov

Expertise: Extensive experience (research and field) on the use of PAM in agricultural irrigation systems. Has conducted extensive studies on the use of PAM and provides important contributions on how PAM would be used in irrigation systems.