THE ENVIRONMENTAL CONCERNS OF ARSENIC ADDITIVES IN POULTRY LITTER: LITERATURE REVIEW

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Prepared for the Harry R. Hughes Center for Agro-Ecology, Inc., an Affiliated Foundation with the University of Maryland, College of Agriculture and Natural Resources in Response to a Request by the Environmental Matters and the Education, Health and Environmental Affairs Committees of the Maryland General Assembly

December 1, 2011

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Abstract:

This review examines the scientific literature on the environmental concerns of arsenic additives in poultry litter. A number of questions were addressed on this issue. In summary, the review found:

1) **Does arsenic from poultry feed amended with roxarsone end up in poultry litter?**

    The arsenic found in poultry feed ends up in the poultry litter. Poultry litter from chickens receiving feed without roxarsone added contains only trace levels of arsenic, generally below detection limits of $\approx$ 1 mg/kg. Once roxarsone is added to the feed, the litter produced by the chickens contains total arsenic concentrations ranging from 2.9 to 77 mg/kg.

2) **If poultry litter contains arsenic, is it present in an organic or inorganic form?**

    Fresh poultry litter contains predominately organic roxarsone while aged litter contains predominately inorganic arsenic (As(III) and As(V)). Roxarsone is converted rapidly to inorganic arsenic both within the litter pile as well as after field application as fertilizer. This conversion is both bacterially mediated and through photolysis. Thus, very little arsenic from poultry litter remains as organic roxarsone after introduction to the environment.

3) **When applied to agricultural fields, does arsenic accumulate in soils to a level of concern based on existing soil arsenic environmental soil criteria?**

    A number of controlled experiments have shown that arsenic accumulates in soils once applied in poultry litter. Soil arsenic levels from litter amended fields are statistically greater than levels from unamended soils. This arsenic is predominately in the form of inorganic arsenic (As(III) and As(V)). Some areas on the Delmarva Peninsula which have received poultry litter for decades have accumulated arsenic to levels above both the Delaware and Maryland soil arsenic background remediation standards. A number of papers indicate that the use of arsenic as a feed additive is not a sustainable practice since arsenic concentrations continue to accumulate over time and soil levels will eventually increase to concentrations above these background remediation standards.

4) Does arsenic transport from litter amended surface soils into shallow aquifers and receiving streams and, if so, are levels high enough to be of concern to the biota in these ecosystems based on existing arsenic environmental criteria?

The arsenic literature indicates that surface applied roxarsone has little influence on groundwater arsenic concentrations on the Delmarva Peninsula. Once applied to soils, arsenic binds tightly and does not transport to these shallow aquifers to any significant extent. Investigation of 508 shallow groundwater sites on the peninsula in the scientific literature reveal only 4 with arsenic concentrations above the current drinking water standard of 10 µg/L. Deep drinking water aquifers are contaminated with arsenic at levels above the current drinking water standard but this appears to be from geological (i.e., natural) sources of arsenic.

The scientific literature makes it clear that once applied to fields in poultry litter, arsenic can be transported from these fields after rain events into surface receiving waters. Transport is predominately as inorganic arsenic. Concentrations of arsenic in field ditches and receiving streams were not found to be above water quality criteria for the protection of aquatic life but were often above criteria for the protection of human health if resident biota was consumed from these areas. The magnitude and number of criteria exceedances were dependent on the criteria employed by the various state and/or federal regulatory agencies, more stringent criteria resulting in more frequent and greater exceedances. One study implicated roxarsone amended poultry litter as being responsible for arsenic stream exceedances in an area dominated by agriculture. Another study indicated transport of arsenic from very shallow groundwater to nearby receiving streams.

5) Are arsenic levels in sediments and biota of Chesapeake Bay at levels of environmental concern?

A recent study conducted in the agriculturally dominated Pocomoke, MD watershed indicated some arsenic levels to be above sediment criteria established by Delaware and the U.S. EPA but not above criteria set by Maryland. An extensive sampling and toxicity study of sediments in the Inland Bays of Delaware indicated that sediment arsenic concentrations were below levels of concern for bottom dwelling organisms.

A recent study of aquatic life in the Inland Bays of Delaware indicated that arsenic within fish and shellfish was largely organic in nature with detections of inorganic arsenic below the method quantitation limit. Organic arsenic is much less toxic to aquatic organisms than inorganic arsenic as is the case in humans.

6) What are background levels of arsenic in Maryland soils and what is the potential for arsenic in poultry litter to alter soil profile arsenic levels relative to other arsenic sources (e.g., atmospheric deposition, biosolids application as fertilizer, etc.)?

An arsenic reference soil background value of 3.6 mg/kg was recently established by the Maryland Department of the Environment. This was calculated for the eastern part of Maryland and is consistent with other studies conducted on the Delmarva Peninsula. As indicated in Question 3 above, soil arsenic concentrations on the peninsula in areas of long-term poultry litter applications can exceed this background concentration.

Atmospheric deposition of arsenic is approximately 300 times less annually than application of arsenic in poultry litter. Biosolids from sewage treatment plants are also used as fertilizer on Maryland's Eastern Shore. In general, concentrations of arsenic in biosolids are less than concentrations in poultry litter. In addition, the arsenic in biosolids appears to be more tightly bound and less water soluble than the arsenic in poultry litter.

7) How are recent changes in phosphorus based nutrient management likely to change arsenic additions to Maryland cropland?

Phosphorus based nutrient management will tend to limit the applications of any waste material that previously was applied at rates that over applied phosphorus relative to crop needs. As a result, rates of arsenic application and rates of arsenic accumulation will tend to decrease in fields where poultry litter was formerly applied at rates well in excess of what was needed to meet crop phosphorus needs. However if the overall amount of arsenic in poultry litter remains constant, phosphorus based nutrient management will not change the total amount of arsenic applied to Maryland cropland unless poultry litter is exported from the state. Another large phosphorus source in Maryland that has increased due to increasing population and increased efficiency of phosphorus removal from human waste streams is biosolids. Similar to the case for poultry litter, phosphorus based nutrient management will reduce biosolids application rates. Since arsenic to phosphorus ratios in biosolids tend to be lower than historic levels in poultry litter, arsenic accumulation in soils will tend to be slower when using biosolids to meet crop phosphorus needs. However, biosolids can be highly variable depending on the treatment system and incoming waste stream so a wide range in arsenic to phosphorus ratios would be expected.

8) What controls the behavior of arsenic after it is applied to soils?

Arsenic in poultry litter is highly water soluble creating potential for short-term losses with water moving across the soil where litter was surface applied, and movement downward through the soil profile immediately after poultry litter application. However, most soils have a high capacity for binding arsenic and most applied arsenic soon becomes unavailable for leaching. Despite most arsenic in surface soils being tightly bound, as surface soils become more enriched in arsenic, the potential for downward movement increases but the movement is limited in most soils due to the high capacity for binding of arsenic to clay minerals and oxides of iron in aluminum in subsoil horizons.

In this review we have attempted to capture all the relevant information available regarding the potential arsenic related environmental impacts in Maryland related to land application of arsenic amended poultry litter. Unfortunately, research on the topic in the mid Atlantic region is relatively limited, and there is considerable variation in the data generated and conclusions drawn in these studies. This inconsistency in findings is likely due to a number of factors including but not limited to the complexity of arsenic chemistry itself, differences in analytical and soil sampling methods, widely varying soil types and background arsenic concentrations, uncertainties regarding historical arsenic concentrations in litter and litter application rates, and possible prior land use impacts on soil arsenic concentrations. Despite the variation in research findings we were able to develop consensus answers to the general questions regarding the forms and concentrations of arsenic in poultry

litter, soil, groundwater and surface waters although some questions remain regarding inconsistencies in findings. However, a more difficult issue is that related to the levels of arsenic in soil and water that pose an environmental threat. Currently there are varying criteria used by the states and the federal government (U.S. EPA) covering arsenic in soil, water and sediment so making judgments regarding what levels of arsenic are problematic depends on the chosen criteria. There is considerable ongoing debate on this topic but generally the discussion seems to be moving toward a more restrictive approach to managing arsenic in the environment. Addressing this aspect of arsenic in the environment was beyond the scope of this review.

Introduction

Roxarsone® is the trade name of an organic compound containing arsenic (4-Hydroxy-3-nitrobenzenearsonic acid) that has been approved by the FDA since 1944 for use in poultry feed individually and in combination with other drugs for disease prevention (e.g., coccidiosis, a parasitic intestinal disease), growth promotion, enhanced feed utilization and improved meat pigmentation (USFDA, 2011). Arsenic is a metallic element that occurs in the earth's crust mostly in inorganic form (National Academy of Sciences, 1977). Due to a number of environmental and human health issues concerning arsenicals, their use was discontinued as feed additives by the European Union in 1999. Although the use of arsenic was not officially banned, maximum permissible limits for arsenic in animal feedstuffs were set sufficiently low that manufacturers stopped selling arsenical amended feed. The limits were set in 1999 at 2 mg/kg for livestock and 4 mg/kg for fish; the fish limit later being increased to 6 mg/kg in 2002 (European Commission, 1999; 2002). For comparative purposes, the recommended concentration of roxarsone in poultry feed in the United States is 25 to 50 mg/kg (Veterinary Medicine Labels, 2011). In addition, since 1990, the conditions for registration and use of animal drugs have been made more rigorous, requiring in particular extensive residue data including development of maximum residue limits (MRLs) of veterinary medicinal products in foodstuffs of animal origin (European Commission, 1990). As a consequence, manufacturers have not sought authorizations for many animal drugs, including roxarsone.

In addition to the European Community's discontinuance of arsenical usage, Perdue Farms, Inc. announced in 2007 that it would no longer use roxarsone or other arsenical feed additives because they found that, through improved flock health programs and housing environments, they were able to produce healthy flocks without roxarsone treatment (Perdue Farms, 2011). In 2009, Perdue Farms, Inc. was ranked the third largest poultry producer nationally according to the Delmarva Poultry industry (DPI, 2011). In 2006 /2007, McDonald's asked its dedicated poultry facilities not to use arsenic additives in their operations (McDonalds, 2011).

During the 2010 legislative session, the Maryland State legislature debated bills (SB 417/HB 754) to ban the use of arsenicals in poultry feed in Maryland. The bills were held over to the next legislative session pending further study on the environmental concerns of using

roxarsone in poultry feed. This literature review is in response to a request by the Environmental Matters and Education, Health and Environmental Affairs committees of the Maryland General Assembly concerning environmental consequences and the sustainability of applying poultry litter containing arsenic to agricultural fields. It should be noted that following the 2010 Maryland legislative session, the U.S. FDA released a controlled study that found a higher incidence of <u>carcinogenic inorganic arsenic</u> in the livers of roxarsone-treated chickens compared to untreated ones (Kawalek et al., 2011). One argument for the safe use of roxarsone is that it remains in an organic form both in the bird and in bird waste and does not transform to inorganic arsenic; the more toxic form. In June 2011, following the release of the U.S. FDA study, the manufacturer of Roxarsone® (Alpharma) suspended the sale of roxarsone in poultry feed.

Arsenic has been determined to be a human carcinogen (IARC, 2004).   Low-level, long-term exposures to arsenic have been shown to cause cancers of the lung, bladder, kidney and skin (Chen et al., 1992; Chen et al., 1988; Wu et al., 1989). Due to these concerns, the USEPA announced that it was lowering the enforceable maximum contaminant level (MCL) for total arsenic in drinking water from 50 µg/L to 10 µg/L (USEPA, 2001). In addition, the literature indicates concerns over chronic, low-level arsenic exposure causing numerous adverse health consequences including cardiovascular disease (Chen et al., 2011; Sohel et al., 2009), type 2 diabetes (Navas-Acien et al., 2008), neurocognitive deficits (Wasserman et al., 2007), adverse birth outcomes (Ahmad et al., 2001) and endocrine disruption (Davey, et al., 2007). The inorganic species (arsenate (As(V) and arsenite (As(III)) are believed to be most potent in inducing toxic effects although the toxic potential of various organic arsenic species (methylated arsenic acids, arsenobetaine, and arsenosugars) is less well studied (National Research Council, 1999; National Research Council, 2001). In one of the few studies on roxarsone, Basu et al. (2008) report angiogenesis or new blood vessel formation associated with vascular disease as well as the growth of new tumors following exposure of human endothelial cell cultures to roxarsone and inorganic As(III). In this study, roxarsone was found to be a more potent inducer of angiogenesis than As(III). This was the first demonstration of functional vascular effects of roxarsone that may implicate a disease risk.

The USEPA's Integrated Risk Information System (IRIS) program is currently reassessing the carcinogenic potency of inorganic arsenic. In February 2010 the draft

reassessment was released for public review and for review by the USEPA's Science Advisory Board (SAB). The comment period for these reviews has been completed but the final reassessment has yet to be released so only the draft document may be cited (found here: http://cfpub.epa.gov/ncea/iris_drafts/ recordisplay.cfm?deid=219111). In the arsenic reassessment, EPA IRIS changed its cancer slope factor (quantitative estimate of increase in cancer risk per unit exposure), a key metric used in cancer risk assessment, from 1.5 per mg/kg-day to 25.7 per mg/kg-day. In lay terms, this means that the USEPA now considers inorganic arsenic to be 17 times more potent a carcinogen than previously believed. Comments from the SAB on the draft document indicate support for the new cancer slope factor. This means that risk assessments establishing acceptable arsenic levels based on the older cancer slope factor may dramatically underestimate cancer risks and will require recalculation using the new slope factor. Further, USEPA IRIS is currently reviewing the enormous body of literature examining the relationship between inorganic arsenic and non-cancer health effects—especially cardiovascular disease. Many researchers with knowledge of arsenic epidemiology believe that the non-cancer health effects are particularly sensitive (i.e. occur at very low chronic exposures), and may actually drive future arsenic risk assessments (Nachman, personal communication). The USEPA IRIS non-cancer arsenic toxicological assessment should be available to the public in late 2012. The above discussion indicates that the more we learn about inorganic arsenic the more of a hazard it appears to be to humans.

In addition to other possible human health issues, a recent publication has shown that homes in Arkansas near fields amended with poultry litter containing roxarsone had elevated arsenic concentrations in dust (O'Connor et al. 2005). Peak dust-associated total arsenic concentrations in the homes ranged from 0.95 to 86.6 mg/kg. Speciation of this dust found roxarsone present, a strong indication that the source of the arsenic was poultry litter. As would be expected from roxarsone degradation pathways in litter (discussed below), the majority of the arsenic was inorganic As(V) with a small percentage of inorganic As(III). The authors felt that the similarities in arsenic species between broiler litter, ambient air particles and household dust was strong presumptive evidence that arsenic was being transported from litter-amended fields through the air and could, therefore, impact persons in nearby areas. The finding of roxarsone in house dusts was the final definitive evidence that broiler litter arsenicals are airborne

contaminants in areas of high density poultry operations. O'Connor et al. recommended that arsenical feed additives should be abandoned due to these direct human health concerns.

The possibility of significant human health consequence generally drives the overall discussion about the risk of continued use of arsenic as a feed amendment, as one would expect. This literature review, however, is concerned specifically with the possible environmental consequences of continued roxarsone use in poultry feed. In 2009 Maryland ranked 8th and 10th, respectively, among all states in terms of number and pounds of broilers produced (DPI, 2011). The majority of this production is on the Delmarva Peninsula, which encompasses the parts of Delaware, Maryland and Virginia east of the Chesapeake Bay. Given the relatively small land area, the Delmarva Peninsula is one of the most concentrated poultry production areas in the United States. As the chickens grow in the poultry houses their excreta is incorporated with the sorbent bedding material (wood shavings, sawdust, etc.) to produce poultry litter. When the houses are cleared, this poultry litter is applied to agricultural fields as organic fertilizer rich in nitrogen and phosphorous. Since roxarsone is used extensively in poultry feed, the Maryland State Legislature sought clarification of the scientific literature concerning the specific environmental issues presented below.

(1) Does arsenic from poultry feed amended with roxarsone end up in poultry litter?

Feed formulations for roxarsone for chickens range from approximately 22.7 to 45.4 gm/ton or 25 to 50 mg/kg (Veterinary Medicine Labels, 2011). There is general consensus in the available scientific literature that poultry fed roxarsone-medicated feed produce a litter that contains arsenic. As very little arsenic remains in the bird, by design, the majority is necessarily excreted. Total arsenic concentrations found in poultry litter vary significantly. Ashjaei (2010) and Ashjaei et al. (2011) measured total arsenic in poultry litters from six Georgia poultry houses and report total arsenic concentrations ranging from 14.9 to 53.4 mg/kg (dry wt.) with a mean (±standard deviation) of 29.8 mg/kg (±13.89 mg/kg). Garbarino et al. (2003) report a mean total arsenic concentration in Kansas poultry litter of 28.7 mg/kg (±0.5 mg/kg) (dry wt.) from birds fed a diet formulation containing roxarsone at 45.5 g/ton. These same authors found a mean total arsenic concentration in Maryland poultry litter of 29 mg/kg (±3 mg/kg) from chickens fed a roxarsone-fortified diet of unknown formulation. This litter was supplied by the Maryland

Agricultural Experiment Station. There is a large body of additional scientific literature showing various concentrations of arsenic in litter, examples include: Sims and Wolf (1994) report litter having total arsenic concentrations 0 to 77 mg/kg, Moore et al. (1998) - 43 mg/kg, Jackson and Miller (1999) – 35.1 mg/kg (dry wt.), Jackson and Bertsch (2001) – 16.79 mg/kg (dry wt.), Sims and Luka-McCafferty (2002) – 45 mg/kg (dry wt.), Jackson et al. (2003) – 15.7 mg/kg (±9.57 mg/kg; range 1 to 39 mg/kg), Toor et al. (2007) – 24 and 43 mg/kg (dry wt.), Han et al. (2004) – 16 samples with a mean of 26.9 mg/kg (±7.8 mg/kg) (dry wt.) ranging from 11.1 to 36.1 mg/kg, Arai et al. (2003) - 47.8 mg/kg (± 2.3 mg/kg)(dry wt.), Adeli et al. (2007) – mean 29.0 mg/kg (±4.41 mg/kg) (dry wt.), Denver et al. (2004) – 27 mg/kg and Codling et al. (2008) – 10 samples with mean 2.93 mg/kg (±0.59 mg/kg) (dry wt.). Codling et al. (2008) noted that the litters they tested were 4 to 10 times lower in total arsenic than litters from other studies. In addition, litter P concentrations for these 10 farms were lower than values reported by other researchers. They thought that the lower concentrations from these specific Maryland Coastal Plain farms could have resulted from the types of bedding material or difference in the feed composition used.

A recent U.S. FDA study measured poultry feed arsenic concentrations before and after the addition of roxarsone (Kawalek et al., 2011). The standard control poultry feed in this study had background levels of total arsenic of 0.156 mg/kg (0.024 mg/kg As(III) and 0.032 mg/kg As(V)) and no detectable roxarsone. After addition of the roxarsone pre-mix, the medicated feed had total arsenic of 11.3 mg/kg (0.023 mg/kg As(III) and 0.036 mg/kg As(V)) and a roxarsone concentration of 11.3 mg/kg. This indicates that the only source of roxarsone to poultry is the roxarsone medicated feed. As discussed in Question 2 on arsenic speciation, organic roxarsone is the predominate species of arsenic found in fresh poultry litter. Thus, poultry litter produced without the addition of roxarsone will have only trace levels of arsenic. Morrison (1969) measured concentrations of total arsenic ranging from 11.8 to 29.6 mg/kg in 11 poultry litters from roxarsone-treated chickens. In all cases where roxarsone was used, roxarsone itself was measured in the litters. Conversely, poultry litter from a house where roxarsone had not been used had a total arsenic concentration of <0.1 mg/kg and no detectible roxarsone was found. Poultry litter samples collected by the Wye Research and Education Center (WREC) from Perdue, Inc had total arsenic concentrations ranging from non-detectable (<1.24 mg/kg) to 17.7 mg/kg (Fisher et al., unpublished data). The samples containing non-detectable arsenic were collected after Perdue had stopped using roxarsone while an earlier sample from this integrator prior to the

discontinuance of roxarsone-amendment contained 17.7 mg/kg total arsenic. This again shows that poultry litter contains only trace amounts of arsenic unless roxarsone is administered as a feed additive.

(2) If poultry litter contains arsenic, is it present in an organic or inorganic form?

Garbarino et al. (2001) found that approximately 70% of total arsenic in a poultry litter sample was water extractible, and that immediately following extraction the main arsenic species present was roxarsone. Under anaerobic conditions and at room temperature, the author reports roxarsone being totally transformed into different arsenical compounds within about 48 hours. The rate of the transformation was positively correlated with temperature; e.g., higher temperature caused accelerated transformation. However, if litter extracts were sterilized, the roxarsone remained stable for a period of at least 10 days. Such findings suggest that microbial processes are responsible for the degradation of roxarsone. Jackson et al. (2003) analyzed 40 poultry litter samples from GA, AL and SC for arsenic following water extraction. Roxarsone was found to be the major species in 50% of the litter leachates. However, the prevalence of As(V) as the major species in the other 50% indicates that roxarsone transforms readily to the more toxic inorganic species. Jackson and Miller (1999) reported that poultry litter from a poultry farm in Athens, GA had a total arsenic concentration of 35.1 mg/kg, with 25.4 mg/kg being water soluble (i.e., 72%). Of this water soluble fraction, 92% was identified as inorganic As(V). However, the authors point out the possibility that an organo-arsenical could have co-eluted with As(V) under their experimental conditions.

Garbarino et al. (2003) conducted extensive experiments examining changes in arsenic speciation in litter over time. The dominate water soluble species of arsenic in fresh dried litter was organic roxarsone (91%). When water was added to the litter and the mixture composted at 40ºC for 3 to 4 weeks, the dominate arsenic species was inorganic As(V). Degradation of organic to inorganic arsenic via composting was time dependant with 90% of the roxarsone converted to inorganic arsenic after 23 days and 100% converted after 38 days. Increasing the amount of water also increased the degradation rates. The authors felt that the degradation was microbially mediated. They also found that litter windrows (an in-house composting technique) from various poultry houses in AK, OK and MD showed that arsenic originally present as

roxarsone had been converted to As(V). Ashjaei (2010) also found that fresh poultry litter contained mostly organic roxarsone while litter stored for 4 months prior to application contained predominately inorganic As(V) with some measurable roxarsone.

Similarly, Rosal et al. (2005) found that almost all of the arsenic measured initially in manure taken from broiler chickens fed a diet containing roxarsone was indeed roxarsone. Once dissolved in water, roxarsone can rapidly undergo photo-degradation in the presence of natural organic matter to the more soluble and toxic inorganic species As(III) and As(V) (Bednar et al., 2003). Jackson and Bertsch (2001) analyzed a poultry litter sample of unknown storage history with a total arsenic concentration of 16.79 mg/kg. Water extracts of this sample contained predominately roxarsone (≈40 µg/L) with measurable concentrations of As(III)(≈0.3 µg/L) and As(V)((≈2.5 µg/L). Jackson et al. (2006) analyzed two poultry litter samples used in their studies on arsenic fate from land applied litter that contained arsenic. Although the history of each litter was not given, one had roxarsone as the dominant species and one had As(V) indicating that different litters can have different arsenic speciation. Cortinas et al. (2006) found that under anaerobic conditions roxarsone was degraded over 75 to 250 days through microbial processes to a number of intermediate arsenic compounds before eventually predominating as inorganic As(III) with some inorganic As(V). In laboratory anaerobic microbial degradation experiments, Stolz et al. (2007) also found that roxarsone in chicken litter was rapidly degraded (204 h) to As (V) and another organic arsenic species (3-amino-4-hydroxybenzene arsonic acid). The microbe involved in this biodegradation was identified as a *Clostridium* species closely related to *Clostridium celerecrescens* which occurs naturally in the gut and feces of chickens. Numerous species of *Clostridium* also colonize the bowel of humans (Todar, 2011). These degradation findings are important because roxarsone may occur in anaerobic environments, such as anaerobic zones of compost and anaerobic sediments.

Although most of the arsenic in fresh poultry litter is in the form of roxarsone, these studies show that the arsenic in roxarsone is converted into one or more inorganic arsenic species (As(III) and As(V)) which are more water soluble and toxic than roxarsone. During storage and especially after land application, poultry litter can be exposed to precipitation, high temperature and sunlight allowing roxarsone to rapidly undergo both photo- and microbial-degradation to these inorganic forms.

(3) When applied to agricultural fields, does arsenic accumulate in soils to a level of concern based on existing soil arsenic environmental soil criteria?

The current Delaware soil arsenic background remediation standard is 11 mg/kg (DNREC, 2007) while the Maryland soil arsenic background remediation standard is 3.6 mg/kg (MDE, 2008) (Table 1).

Kingery et al. (1994) and Han et al. (2000) found significantly elevated levels of the heavy metals copper and zinc in surface soils (10-15 cm) amended with poultry litter for approximately 25 years compared to non-littered soils. Although arsenic was not measured in these experiments, they do show that trace metals can significantly accumulate in soils following long-term applications of poultry litter. Han et al. (2004) measured surface (0-5 cm) soil arsenic concentrations in a field amended with poultry litter for 25 years and in a forested area that had never received litter amendments. Arsenic in the soils from the litter amended field had a mean total arsenic concentration of 8.4 mg/kg (±3.5 mg/kg)(dry wt.) while soils from the forest had mean total arsenic of 2.68 mg/kg (±1.35 mg/kg). Arsenic in the long-term amended soils appeared to be in more stable residual forms compared to poultry waste itself, which contained arsenic in the more water soluble form. The authors state that this indicated possible "quick leaching" of water-soluble arsenic into surface waters after litter was applied to the fields.

Arai et al. (2003) sampled soils from 4 sites in Delaware that had received poultry litter application for 3 to 4 decades. Soils sampled from the four sites ranged in arsenic concentration from 12.0 to 15.0 mg/kg. Inorganic arsenic species (As(II, III and V)) were found in all of the soils. Although these authors state that the arsenic concentrations found in the soils did not indicate long term accumulation compared to arsenic concentrations common in litter, all of the values reported were above the current Delaware soil arsenic background remediation standard of 11 mg/kg and were well above the lower Maryland background remediation standard for soils of 3.6 mg/kg.

Gupta et al. (1999) measured total acid extractible (HNO_3) arsenic in soil from three cultivated, long-term litter amended fields and three unamended wooded areas in Wicomico County on the Eastern Shore of Maryland. They measured arsenic at depths to 60 cm in 10-cm increments. At all depths except 20-30 cm, total arsenic in the amended soils was significantly

greater than in the unamended areas (e.g., at a depth of 50-60 cm total arsenic concentration was 9.43 mg/kg (dry wt.) in field soils compared to 5.5 mg/kg in the unamended forested areas).

Rutherford et al. (2003) found that water extractable arsenic in surface soils (0-15 cm) increased after one-year application of poultry litter at 6 tons/acre and after two years at both a 3 and 6 ton/acre application rate. Two applications of litter caused a 2 to 3 fold increase in water soluble arsenic compared to plots receiving no litter. The litter for this study was provided by Garabino et al. (2003) and contained predominately As(V). No litter had been applied to these plots prior to this 2 year experiment. These authors also examined soils from Delmarva that had been amended with poultry litter for long periods of time and compared them to similar soils from forested areas that had not received litter. Water-extractable arsenic was more than six times higher in the litter-amended Delmarva soils than in the unamended forest soils. Water extractable arsenic decreased with sample depth while acid-extractable total arsenic and iron (Fe) increased with depth in the amended soils. Concentrations of total arsenic were approximately twice as high at all depths in the amended soils compared to the unamended soils. The strongly bound arsenic fraction (i.e., acid extractible) correlated positively with Fe in amended fields. The authors suggest that there might be sorption or co-precipitation of arsenic and Fe in the soil columns.

Codling et al. (2008) found that soils from ten farms on the Maryland coastal plain with a history of litter application had higher levels of total arsenic than forested soils from the same region. Arsenic concentrations in the litter amended soils ranged from 0.6 – 3.0 mg/kg (dry wt.) compared to concentrations in the forested soils of 0.14 – 0.59 mg/kg. This indicates a buildup of arsenic in soils over time following poultry litter amendment (although final levels were still below the 3.6 mg/kg MD soil remediation standard). It is interesting to note that the poultry litter collected from these farms was ≈10 times lower in arsenic (2.93 mg/kg ($\pm$0.59 mg/kg)) than in litters reported in other publications (See the discussion in Question 1 above on this difference reported by Codling et al., 2008). Adeli et al. (2007) also found increases in soil total arsenic concentration after applying poultry litter containing arsenic (mean 29.0 mg/kg ($\pm$4.41 mg/kg)(dry wt.)) for three years to cotton fields in Mississippi. Litter application rates varied between 0 and 6.7 Mg/ha (1 Mg(megagram)/ha = 0.45 tons/acre). Unamended soils contained total arsenic between 0.16 and 0.44 mg/kg prior to the study. Under the no-till system,

application of broiler litter at the highest rate (6.7 Mg/ha) significantly increased soil surface (0–15 cm) total arsenic by 69% compared with unfertilized control soil. The highest measured total arsenic concentration in the soils was ≈6.6 mg/kg (interpreted from their figures). Adeli et al. concluded that broiler litter application to cotton over three years may not currently pose any environmental threat from trace elements but sustained application at rates sufficient to satisfy required N would result in increased trace element accumulation over time.

Ashjaei (2010) and Ashjaei et al. (2011) reported that soil total arsenic concentrations in 0.8 ha (hectare) plots in GA receiving litter amendment were significantly higher at two soil depths and series (Cecil and Sedgefield) than in unamended control soils. The treatment plots had been amended with litter at 5 Mg/ha (≈2.2 tons/acre) from 1995 through 2009. All plots were planted with tall fescue (*Festuca arundinacea Scherb*) and Bermuda grass (*Cynodon dactylon L.)*. Total concentration of arsenic was significantly greater in PL-amended Cecil and Sedgefield soils (3.67 mg/kg and 3.91 mg/kg (dry wt.), respectively) compared to those in control plots (1.46 mg/kg) at 0-2.5 cm depth. Similar results were found for total arsenic concentrations in both litter-amended soils compared to those in control plots at 2.5-7.5 cm depth. There were no differences in total arsenic concentrations between the two litter-amended soil series at either depth. The total arsenic soil concentrations were below the current Delaware soil arsenic background remediation standard of 11 mg/kg, but at or above the Maryland standard of 3.6 mg/kg. Ashjaei (2010) conclude that it is clear that the practice of using arsenic in animal feeds is not sustainable, for the simple reason that arsenic will continue to accumulate in soils over time. The author also found that there were significantly higher arsenic concentrations in grasses grown on the roxarsone-amended fields compared to the control fields although the average tissue arsenic concentrations in the two grasses (0.23 and 0.31 mg/kg) remained well below the maximum tolerance levels of arsenic for cattle and sheep feed of 30 mg/kg (National Research Council, 2005).

Sparks et al. (2007) published an extensive report on the fate and transport of arsenic in Delaware soils. One objective was to obtain soil profile samples from benchmark soil series throughout Delaware to determine the effects of past land uses, soil type, and especially agricultural management practices (e.g., manure use, cropping systems) on soil arsenic levels. Of particular interest were comparisons between settings where broiler litter had been applied at

different frequencies (e.g., not at all; every year; and one-year in a three-year crop rotation) and forested areas adjacent to cropland receiving litter. Unfortunately, difficulties securing access to broiler litter-impacted soils resulted in a limited number of farms being sampled. To compensate for this, the authors obtained additional soil samples from five University of Delaware (UD) farms in New Castle and Sussex counties. These UD soils had a diverse history of cropping practices and past manure/fertilizer use. Total arsenic concentrations in the 22 benchmark soil series located on agricultural and forested lands (86 surface and subsoil samples) averaged 4.7 mg/kg (± 3.5 mg/kg)(dry wt.), below the current proposed Delaware soil arsenic background remediation standard of 11 mg/kg, but again, well above the MD standard of 3.6 mg/kg.

Closer examination of the Sparks (2007) report indicates some interesting data. Forested soils in Sussex County that had not received poultry litter amendments had a mean total arsenic concentration of 2.6 mg/kg (± 1.9 S.D.)(range: 0.2 to 6.1 mg/kg). Agricultural soils from cooperators in Sussex County had a mean total arsenic concentration of 2.6 mg/kg (±1.8 S.D.) (range: below detection to 6.6 mg/kg) while soils from New Castle County had a mean total arsenic concentration of 4.1 mg/kg (± 1.9 S.D.)(range: 2.1 to 9.2 mg/kg). Meanwhile, the five UD farm soils had higher mean total arsenic concentrations: 1) Sussex Co. - 4.32 mg/kg (± 2.5 mg/kg)(range: 0.4 to 8.9 mg/kg); 2) New Castle Co. - 6.7 mg/kg (± 2.5 mg/kg)(range: 0.4 to 8.9 mg/kg); 3) New Castle Co. - 8.7 mg/kg (± 4.83 mg/kg)(range: 3.3 to 19.6 mg/kg). Since the history of poultry litter application on these farms varied, it is difficult to establish with certainty what specific practice(s) produced the higher arsenic concentrations in UD New Castle farms. The New Castle Co. UD farms did have four total arsenic values above the current Delaware soil arsenic background remediation standard of 11 mg/kg. Many soil samples from the UD farms and elsewhere within the state were above the lower Maryland background concentration of 3.6 mg/kg.

Sparks et al. (2007) calculated future arsenic accumulation in DE soils based on realistic arsenic application and loss scenarios to estimate eventual build up. They assumed an average total arsenic concentration of 40 mg/kg in poultry litter, a litter application rate of 9 Mg/ha, broiler litter application two years out of three, as might occur in a corn-soybean-corn rotation, and loss of 10% added litter arsenic from topsoils though erosion, leaching, plant uptake, or volatilization. In this scenario, it would require 75 years before topsoil total arsenic would be

>11 mg/kg, the Delaware reference soil background concentration (Table 1). Much less time would be required to produce exceedances if the Maryland background level of 3.6 mg/kg were used. The authors state that application of broiler litter at agronomic rates could increase soil total arsenic values above the Delaware Department of Natural Resources and Environmental Control (DNREC) arsenic standard within one or two generations raising questions about the sustainability of arsenic use in poultry production. A sustainable practice is generally assumed to be one that can be continued indefinitely with no adverse environmental effects. Based on the current criteria used by DNREC to identify soils where total arsenic is of environmental and ecological concern (11 mg/kg), their calculations and field data suggest that it would be prudent to investigate alternatives to the use of roxarsone or other organo-arsenicals in poultry production.

(4) Does arsenic transport from litter amended surface soils into shallow aquifers and receiving streams and, if so, are levels high enough to be of concern to the biota in these ecosystems based on existing arsenic environmental criteria?

The Maximum Contaminant Level (MCL) for drinking water established by the U.S. EPA and adopted by the states of Maryland and Delaware is 10 µg/liter (USEPA, 2001). The current arsenic (inorganic) water quality criteria for the protection of aquatic life were first published in 1984 and despite additional research on the acute and chronic toxicity of arsenic to aquatic organisms have not been changed since (USEPA, 1984) (Table 2). Maryland and Delaware both use the USEPA arsenic water quality criteria to establish permissible state water quality levels. For freshwater the criteria for protection from acute and chronic toxicity are 340 µg/L and 150 µg/L, respectively. Acute and chronic saltwater criteria are lower at 69 µg/L and 36 µg/L, respectively. For comparison, Canada has more recently established arsenic criteria of 5.0 µg/L for freshwater and 12.5 µg/L for marine systems (CCME, 2001). Maryland and Delaware water quality criteria for the protection of human health for fish consumption are 1.4 µg/L and 10 µg/L, respectively (Table 2). The equivalent USEPA criterion for fish consumption is significantly lower at 0.14 µg/L (Table 2).

The arsenic literature indicates that surface applied roxarsone has little influence on groundwater arsenic concentrations. In 2000 the U.S. Geological Survey published a report on the occurrence of arsenic in groundwater resources of the United States (1980s and early 1990s)

(Focazio et al., 2000). A total of 298 samples were from the DE and MD Eastern Shore counties. Approximately 200 of the wells sampled were from depths ≤ 100 ft. (range: 2 to 100 ft.). The highest total arsenic concentration measured in these shallow wells was 9 µg/L (well depth 90 ft.), slightly below the Maximum Contaminant Level (MCL) in drinking water of 10 µg/liter. Of the 200 shallow wells, total arsenic was ≤ 4 µg/L in 99.5%, and ≤ 1 µg/L in 87%. Greene (2010) reported on arsenic sampling in shallow groundwater wells by the Delaware Department of Agriculture at 164 Delaware sites between 2001 and 2003. Ninety-nine percent of these samples had arsenic concentrations <10 µg/L while 97% had levels < 5 µg/L. Only 2 samples had arsenic concentrations above 10 µg/L, one at 12 µg/L and one at 33 µg/L. When resampled in 2010 this higher well had an arsenic concentration of 15.8 µg/L. Specific information on well depth was not provided, but the author indicated they were "10s" of feet rather than "100s" of feet deep. Denver et al. (2004) conducted a reconnaissance for arsenic on the Delmarva Peninsula, including a special study in the Pocomoke watershed, a poultry-dominated agricultural area on the peninsula. Of 19 shallow groundwater samples from the Pocomoke, only 1 had a total arsenic concentration greater than 10 µg/L (23 µg/L, range <0.1 to 23 µg/L). The sample depths for these wells ranged from 4 to 50 ft. The well with the arsenic concentration of 23 µg/L had a depth of 6 ft. Twenty-nine deeper groundwater samples from major aquifers throughout the Delmarva Peninsula had measurable arsenic of <10 µg/L (range; 1.0 to 7.6 µg/L).

In a very recent report, the Maryland Geological Survey of the MD Department of Natural Resources examined arsenic data from more than 4,200 wells to determine the geographic distribution of arsenic in the Coastal Plain aquifers of Maryland (Drummond and Bolton, 2010). These data indicate that the Aquia and Piney Point aquifers are the only Coastal Plain aquifers with water that exceeds the MCL in drinking water of 10 µg/L on a widespread basis. Inorganic arsenite (As(III)) was the dominate dissolved species measured with some arsenate (As(V)) and very low concentrations of the organic species monomethyl-arsonate and dimethyl-arsenite. There were no exceedances of the MCL in the Potomac, Magothy, or Columbia (surficial) aquifers, and only one MCL exceedance in a well from the Miocene (shallow) aquifer. Of the approximately 120 wells sampled in the shallowest aquifers on the Eastern Shore (Miocene and surficial Columbia) only one had an arsenic level of >10 (Pocomoke well number WO Fs 60 (≈200 ft.); total arsenic concentration of 14 µg/L). Wells as shallow as 40 ft. were sampled in this survey. The authors state that "The lack of elevated arsenic

concentrations in the shallow aquifers, the age of water in the Aquia and Piney Point aquifers, and the distribution of arsenic in the Aquia and Piney Point aquifers indicate that the overall arsenic occurrence is a natural phenomenon, and is not caused by anthropogenic contamination".

Recent shallow groundwater sampling conducted on a 33-acre experimental watershed at WREC in Queenstown, MD indicates very low levels of arsenic (Fisher et al., unpublished data). The five wells sampled on the No-till experimental watershed were all less than 15 ft depth. This research field had poultry litter applied 8 times since 1998. The litter arsenic concentrations from the 5 litter applications, between 1998 to 2002, ranged from 27.4 to 31 mg/kg. Litter in applications from 2008 to 2010 came from Perdue, Inc. who had stopped using roxarsone by that time so arsenic concentrations were non-detectable (< 1.24 mg/kg). Shallow groundwater total arsenic concentrations in the five wells ranged from 0.50 to 1.18 µg/L, all well below the drinking water MCL of 10 µg/L and indicating little or no transport of arsenic to shallow groundwater in this experimental watershed.

The preceding five references indicate that shallow groundwater arsenic concentrations greater than the MCL of 10 µg/L are very infrequent. Of the 508 sites sampled for these studies only 4 had total arsenic above the MCL (0.8%). One was a sample from 200 ft. which cannot be considered as shallow groundwater. It follows logically that if deep aquifer drinking water was extensively contaminated by surface applied roxarsone, shallow water aquifers would be similarly or perhaps more seriously contaminated. That this relationship has not been found to exist suggests minimal influence of surface application of arsenic to groundwater. It should, however, be noted that depths for samples from many of these studies are not provided, and comparatively few may actually be from shallow groundwater where a more profound impact would be expected. Additional investigation in this area may still be warranted.

The scientific literature makes it clear that once applied to fields in poultry litter, arsenic is able to runoff into receiving waters. As discussed in Question 2, most if not all arsenic in runoff is in a water-soluble inorganic form, either as As(III) or As(V). Moore et al. (1998) conducted poultry litter runoff experiments using rainfall simulators on small fescue experimental plots. Poultry litter used in the experiments contained 43 mg/kg total arsenic and was applied at various application rates ranging from 1 to 4 tons/ac. These application rates

were all below the maximum recommended rate at the time of 5 tons/acre. Runoff was collected in troughs at the down-slope end of each plot. Immediately following the first simulated runoff event, total dissolved arsenic concentrations increased significantly and in dose-dependent manner with the highest concentration (224 µg/L total arsenic) occurring at the highest litter application rate. A second runoff event 7 days later on the same fields resulted in a dissolved arsenic concentration of 91 µg/L. On this occasion there was no significant correlation with application rate. For comparative purposes, total arsenic concentrations in runoff from the unamended control plots were 28 and 31 µg/L for the first and second simulated rain events, respectively. These runoff concentrations were well below the water quality criteria for the protection of freshwater aquatic life, but only marginally below the criteria for saltwater aquatic life (Table 2). The arsenic concentrations in runoff were higher than those reported elsewhere on the Delmarva Peninsula for receiving streams as reported for Denver et al. (2004) (discussed below). The major difference was that these arsenic values were direct field discharges and not receiving stream measurements.

Ashjaei (2010) conducted rainfall simulation runoff studies to measure the transport of arsenic from test plots after amendment with poultry litter from chickens fed roxarsone. Three different application rates were studied and runoff was measured following rain simulations at 0, 1, 2 and 4 weeks. Litter arsenic concentrations ranged between 21.8 and 53.4 mg/kg (dry wt.). Total arsenic concentrations in runoff from rainfall simulations immediately after litter applications ranged from 37 µg/L to 83 µg/L and were correlated with litter arsenic concentrations. All of the samples taken from these initial runoff events had arsenic concentrations well above the Maryland and Delaware water quality criteria for the protection of human health for fish consumption of 1.4 µg/L and 10 µg/L (Table 2) but none were above the water quality criteria for protection of aquatic life in freshwater. Concentrations of arsenic in runoff decreased in subsequent rainfall simulations but remained elevated well above 10 µg/L (range 22 to 48 µg/L) even 4 weeks after litter application. The author demonstrates that a month between litter application and precipitation was not effective in reducing the concentration of arsenic in runoff below regulatory limits. Arsenic concentrations in all runoff samples were statistically greater than the control field arsenic concentration of 0.21 µg/L. Arsenic species measured in runoff from these various simulations revealed a relationship with the length of time the litter had been held prior to application. Runoff from the application done with fresh litter

contained predominately organic roxarsone while runoff from the aged litter applications contained predominately inorganic As(V). The author obtained similar results by conducting a field-plot scale (0.8 ha) runoff experiment using natural rainfall. Again, the highest arsenic concentrations were in runoff following a rain event 3 days after litter application (average of 23 µg/L). Over subsequent runoff events, arsenic concentrations decreased progressively for all litter-amended soils to levels of only 1-2 µg/L, but were still higher than those from control plots. This continued leaching of arsenic from poultry litter-amended fields is consistent with the findings of Williams et al. (2003) who describe complex soil kinetics causing greater mobility of As(V) than is predicted from simple linear partitioning models. They report arsenic leaching over a relatively long period of time and thus entering receiving streams in runoff many months after field application. The authors also found that, in the presence of higher levels of phosphate, As(V) becomes increasingly mobile indicating greater leaching potential to receiving streams and hence greater potential for environmental problems in regions with extensive phosphate enrichment.

Studies conducted during the summer of 2011 on adjacent 33-acre experimental watersheds at WREC also show the potential for long-term arsenic leaching from fields following poultry litter application (Fisher et al., unpublished data). Litter was applied to a No-till watershed and a watershed managed using a prototype sub-surface litter injector designed to bury litter below the surface in order to reduce the runoff of water soluble contaminants from poultry litter amended fields. Litter was applied during the week of May 23, 2011 to both watersheds. Due to the lack of sufficiently dry litter from one area, two different sources from the same poultry farm were used. The litter applied to the No-till watershed contained 15.6 mg/kg total arsenic while litter applied to the subsurface watershed contained 23.1 mg/kg. The first runoff from these watersheds occurred on July 8, 2011. Runoff from the No-till watershed contained an average total arsenic concentration of 4.5 µg/L (±1.61 µg/L) while runoff from the subsurface watershed contained 1.4 µg/L (±0.21 µg/L). The majority of arsenic (77%) in the runoff was inorganic As(V) while the rest was inorganic As(III). A second smaller rain event on August 14, 2011 resulted in runoff from the No-till watershed containing 3.7 µg/L arsenic while runoff from the subsurface watershed contained only 1.5 µg/L arsenic. This indicates that arsenic continues to transport from these watersheds even 3.5 months after application. It also indicates the potential of the litter application via subsurface injection to significantly reduce the surface

transport of arsenic from litter-amended fields although the arsenic would remain in the soils of these fields.

Church et al. (2010) reported on arsenic in litter amended soils and barn areas and from ditch flows on a research farm at the University of Maryland Eastern Shore (UMES). The poultry farm and adjoining agricultural fields had functioned as a commercial broiler operation for the 25 years immediately prior to its purchase by UMES in 1997. The authors describe the soils as heavily enriched with phosphorous as a result of their long history (35 yrs) of receiving poultry litter (Kleinman et al., 2007). This phosphorous enrichment will affect the movement of arsenic in the soils and may be representative of many agricultural areas on the Delamarva Peninsula with similar histories of litter application. During the period of this study (2005-2007), the farm included three broiler houses and a litter storage shed. Broilers were occasionally raised on the farm, and litter was stored temporarily in the shed before application to farm soils at a rate of 3.3 Mg/ha. Soils were fertilized to meet corn nitrogen requirements using either poultry litter generated from the farm or liquid ammonia. Manure application at the farm occurred in early April of 2005 and 2006. The total arsenic concentration in the litter applied was 2.2 mg/kg, very low compared to roxarsone-amended litters generally used (Question 1). Areas monitored for this study included poultry litter amended fields and areas around the poultry barns and the litter storage shed. The highest total arsenic concentrations in soils were found in association with the litter storage shed, presumably a consequence of spilled litter. Total arsenic concentrations in soils in the immediate vicinity of the shed were more than double the concentrations in field soils (0.91 mg/kg vs the mean for all fields of 0.31 ± 0.05 mg/kg).

Church et al. (2010) also measured arsenic concentrations in ditches on the research farm during rain events in 2005 through 2007. Annual arsenic concentrations in ditches draining from the litter applied fields averaged <3 µg/L. In contrast, arsenic in effluents from ditches draining both fields and poultry barns was more than twice as high (average of 7 µg/L; high of ≈30 µg/L) while effluent in the ditch draining fields, poultry barns and the litter shed had arsenic concentrations between four and eight times greater (12 µg/L and 26 µg/L; highest ≈42 µg/L). The authors state that average annual arsenic concentrations for both years studied exceeded the US EPA MCL for arsenic in drinking water of 10 µg/L. Comparison to the drinking water

MCLs is somewhat misleading because no streams or rivers on Maryland's Eastern Shore are used as drinking water (MDE, 2011a). When compared to the water quality criteria for the protection of aquatic life for freshwater (Table 2), none of the reported values were exceedances (acute criteria = 340 µg/L; chronic criteria = 150 µg/L). When compared to the water quality criteria for the protection of human health for fish consumption from these waters for both Delaware (10 µg/L) and Maryland (1.4 µg/L) many of these total arsenic values were exceedances (Table 2). This comparison must be made with caution because the fish consumption protection numbers are based on inorganic arsenic while only total arsenic was measured by Church et al. It is also notable that the runoff concentrations in these ditches were higher than those reported elsewhere on the Delmarva Peninsula for receiving streams as reported in Denver et al. (2004) (discussed below). The major difference was that these high arsenic values were measured in ditch flows (i.e., comprised entirely of farm generated runoff without dilution) and not receiving streams. No such measurements were made by Church et al. from the low order streams receiving these ditch flows.

Denver et al. (2004) conducted a survey on water quality in the Delmarva Peninsula. Deeper aquifers were sampled for total dissolved arsenic throughout the Delmarva. An additional special study within the Pocomoke watershed was conducted to measure total dissolved arsenic in shallow soil porewater, shallow groundwater, stormwater runoff, and receiving streams and the movement of this arsenic from shallow groundwater through streambeds to the aquatic system. This area has a predominately agricultural land-use including a long history of significant arsenic-amended poultry litter application. As discussed previously, groundwater arsenic concentrations were generally low throughout the Delmarva and in the Pocomoke watershed in particular; most <10 µg/L. Total dissolved arsenic concentrations from shallow soil porewater (collected from shallow soil cores) ranged from 6.8 to 29 µg/L. Total filtered dissolved arsenic in streams during base-flow conditions ranged from 0.5 to 1.6 µg/L while storm-flow total dissolved arsenic ranged from 0.5 to 10.4 µg/L. The highest arsenic concentration (10.4 µg/L) was found in a very small in-field ditch where manure had been applied. Two other samples from this ditch in 1999 and 2000 had arsenic concentrations of 0.50 and 0.51 µg/L. Although several of these dissolved arsenic concentrations were above the drinking water MCL (10 µg/L), this is a somewhat misleading comparison since no streams or rivers on the Eastern Shore are used for drinking water (MDE, 2011a). None of the arsenic

stream values measured by Denver et al. (2004) exceeded the water quality criteria for the protection of aquatic life (Table 2). Some of these arsenic stream concentrations did exceed the Maryland water quality criteria for the protection of human health from fish consumption of 1.4 µg/L (Table 2). These aquatic life and human health criteria were determined for inorganic arsenic while this sampling effort only measured total arsenic. The comparison is still valid however since dissolved arsenic in surface waters has generally been found to be predominantly inorganic. For example, Nice et al. (2008), in an extensive sampling and monitoring effort in the Patuxent River found most dissolved arsenic within oxic waters was inorganic As(V), although in some cases dissolved inorganic As(III) comprised as much as 50% of total arsenic.

Denver et al. (2004) also measured movement of arsenic from shallow groundwater into streams using piezometers in streambeds in the Pocomoke watershed. A total of five streams were sampled. Dissolved arsenic in four of these streambeds ranged from non-detect (<0.1 µg/L) to 4.2 µg/L. In a streambed piezometer transect taken from the North Fork of Green Run near Whitesville, DE dissolved arsenic concentrations ranged from 2.2 to 18.4 µg/L, indicating the possibility of transport of dissolved arsenic from shallow groundwater to the stream at levels high enough to be of concern based on the water quality criteria for the protection of human health in Delaware (10 µg/L; Table 2). Seven of the ten samples taken in this transect had dissolved arsenic levels equal to or greater than 10 µg/L. This was the same drainage basin that had the highest dissolved arsenic concentration measured in shallow groundwater (23 µg/L at a depth of 6 ft.).

Greene (2010) reported on results from an extensive arsenic ambient water sampling effort in the Delaware Inland Bays. Ambient water samples were collected between 1998 and 2008 at 42 stations. A total of 1,624 samples were analyzed for total arsenic and 1,146 for dissolved arsenic. The marine water quality criteria for the protection of aquatic life for Delaware, Maryland and the U.S. EPA is 36 µg/L as inorganic arsenic (Table 2). None of the samples analyzed were above this criteria so aquatic life should not be affected. When compared to the Delaware water quality criteria for protection of human health of 10 µg/L (Table 2) based on fish consumption, there were nine exceedances. The highest level recorded was 28.2 µg/L. The authors indicate that seven of these exceedances may reflect roxarsone usage in poultry litter plus natural background. The number and magnitude of surface water arsenic exceedances are

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worse when human health criteria are employed (Table 2). For example, the Maryland human health criterion for fish consumption is 1.4 µg/L while the equivalent U.S. EPA criterion is 0.14 µg/L. These lower criteria are questioned by personnel at DNREC who believe an inappropriate bioconcentration factor (BCF) was applied in calculating the criteria. Specifically that the BCF does not reflect the ratio of inorganic arsenic in fish to inorganic arsenic in water (Richard Greene, 2011, personal communication). EPA acknowledges this potential problem and allows Delaware's interim criterion of 10 µg/L pending additional review. As can be seen by this discussion, arsenic water quality criteria are in a state of flux and are therefore a bit of a moving target, especially in light of new research linking chronic arsenic exposure with numerous human health issues.

(5) Are arsenic levels in sediments and biota of Chesapeake Bay at levels of environmental concern?

Federal and state sediment arsenic criteria can be found in Table 3. The Maryland sediment criterion of 70 mg/kg is much higher than either the Delaware criterion of 8 mg/kg or the U.S. EPA Region 3 criteria of 9.8 mg/kg for freshwater and 7.24 mg/kg for marine waters. In a study of sediments sampled from streambeds in the Pocomoke watershed, total arsenic concentrations ranged from 0.3 to 17 mg/kg (Denver et al., 2004). Total arsenic in some of these samples exceeded DE and EPA sediment criteria, although none approached the MD standard.

Greene (2010) reported on results from an extensive arsenic sediment sampling effort in the Delaware Inland Bays. Over 167 surface sediment samples were collected between 1990 and 2006. As mentioned above, Delaware has a sediment criterion of 8 mg/kg dry weight. Sediment total arsenic concentrations in this study ranged from 0.125 to 17 mg/kg with ≈ 56 (34%) exceeding the 8 mg/kg state criterion. However, Delaware also uses an Equilibrium Partitioning method to predict porewater concentrations of arsenic with calculated porewater arsenic concentrations then compared to the appropriate water quality criteria listed in Table 2. DNREC feels this is a better indicator of benthic exposure because it incorporates estimates of arsenic bioavailability. When sediment concentrations were adjusted using this Equilibrium Partitioning method, all porewater arsenic concentrations were found to be well below the water quality criteria. For corroboration of these findings, sediment toxicity tests were conducted on 142 of the sediment samples. Only 3 samples were found to be toxic and this toxicity was purported to

be caused by ammonia or H_2S. From these studies, the DNREC has concluded that arsenic in Delaware Inland Bays poses little threat of toxicity to sediment biota. This work was specific to inland bays and thus cannot be applied more generally to the freshwater streams that might be more abundantly impacted by runoff from poultry litter amended fields. To our knowledge, this is the only large scale study of arsenic in aquatic sediments on Delmarva. However, the smaller study by Denver et al. (2004) found very similar concentrations of total arsenic in sediments in the Pocomoke watershed of Maryland.

There is very little literature on arsenic levels and speciation in biota on the Delamarva Peninsula. One recent study reported the total concentration and chemical speciation of arsenic in edible tissue of several marine fish and shellfish collected from the Delaware Inland Bays and the Delaware estuary (Greene and Crecelius, 2006). Of the 28 samples analyzed total arsenic ranged from 0.360 to 3.33 µg/g. Inorganic arsenic was not measured above the method detection limit (0.03 µg/g) in any samples. Four samples indicated a presence of inorganic arsenic above the procedural black concentration (0.006 µg/g) but below the method detection limit. The authors indicate that, since the organic species of arsenic are relatively nontoxic compared to inorganic arsenic and the inorganic arsenic concentrations were barely detectable, these fish and shellfish arsenic concentrations do not warrant a fish consumption advisory. For example, arsenobetaine, the predominant organic arsenic compound in fish, has an LD50 of >10 g/kg in mice (Kaise and Fukui, 1992). It also appears that arsenobetaine is not accumulated or metabolized by humans but rather is eliminated rapidly as arsenobetaine (Brown et al., 1990; Lai et al., 2004). A recently released U.S. EPA report on contaminant levels in fish fillets from freshwater lakes found similar results to Greene and Crecelius (2006)(US EPA, 2009). Total inorganic arsenic was rarely detected in predator fish (< 1% of the sampling sites) or bottom dwelling fish (9% of the sampling locations). The minimum detection limit and the minimum quantitation limit for total inorganic arsenic was 0.03 µg/g and 0.1 µg/g, respectively. For the 486 predator samples, no total inorganic arsenic concentrations were above the minimum quantitation limit while for the 395 bottom dwelling samples only 6 were above the minimum quantitation limit.

(6) What are background levels of arsenic in Maryland soils and what is the potential for arsenic in poultry litter to alter soil profile arsenic levels relative to other arsenic sources (e.g., atmospheric deposition, biosolids application as fertilizer, etc.)?

Maryland Department of the Environment (MDE) recently conducted a study of soils around the state to document soil background levels as a necessary step to establish standards for soil remediation efforts (MDE, 2008). For soils in the eastern part of Maryland, this background arsenic concentration averaged 2.3 mg/kg (±1.2 mg/kg; range 0.12 – 6.9 mg/kg; N=76). A value defined as the "Anticipated Typical Concentration" (ATC) represents a reference or background level for a given analyte, in this case arsenic, and reflects the mean of measured concentrations plus one standard deviation. In this way the ATC is reflective of variance among samples and also necessarily equals or exceeds the majority of measured background sample concentrations. An arsenic ATC reference background value of 3.6 was calculated based on the recent MDE survey of arsenic in eastern Maryland soils (Table 1).

Fisher et al. (unpublished data) collected soil samples from the WREC research watersheds in 1992 and 1998 prior to any application of arsenic-amended poultry litter. The average soil background level on these Delmarva Peninsula agricultural fields was 2.3 mg/kg (±0.66 mg/kg; range: 1.2 – 3.6 mg/kg; n=44). These results were very similar to those from the MDE study for other eastern shore soils. For additional comparison, forested soils in Sussex County, DE on the Delmarva Peninsula that had not received poultry litter amendments had a mean total arsenic concentration of 2.6 mg/kg (±1.9 mg/kg)(range: 0.2 to 6.1 mg/kg)(Sparks, 2007). Considered collectively, these background values representing a large area (both on Delmarva and from portions of eastern Maryland on the western shore) and reflecting differing soil types are surprisingly similar. The Maryland ATC (3.6 mg/kg) serves as the soil background remediation concentration. Delaware uses a higher soil arsenic background remediation concentration of 11 mg/kg (Table 1).

As discussed in Question 3, the bulk of the scientific literature reports that application of poultry litter with roxarsone results in increases in arsenic concentration in soils relative to soils that are not amended with roxarsone. For example, Arai et al. (2003) reported total arsenic concentrations ranging from 12 to 15 mg/kg (dry wt.) at four sites in Delaware that had received roxarsone amended poultry litter for four decades. Gupta et al. (1999) found arsenic levels in three long-term litter amended fields as high as 9.4 mg/kg (dry wt.). Sparks et al. (2007) did an

extensive analysis of Delaware soils for arsenic. Soils from a forested area that had never received litter had an average total arsenic concentration of 2.6 mg/kg (dry wt.); very similar to background soil arsenic concentrations in Maryland discussed previously. Agricultural soils from farms in Delaware that had received poultry litter in the past ranged in average arsenic concentration from 2.6 mg/kg (±1.8 mg/kg) to 8.7 mg/kg (±4.83 mg/kg) with a high value of 19.6 mg/kg. Sparks et al. (2007) questioned the sustainability of the application of roxarsone amended broiler litter at present agronomic rates due to the slow but steady accumulation of arsenic in the amended soils.

Atmospheric deposition is another source of arsenic to Delmarva soils. Scudlark and Church (1988) measured total bulk (wet plus dry) atmospheric deposition of arsenic in 1985 and 1986 at Cape Henlopen State Park in Delaware. They found an average arsenic deposition of 0.43 $\mu g/m^2$/day. In a follow up study that incorporated data from their earlier work, Scudlark et al. (1994) measured average long-term bulk arsenic deposition at the same Cape Henlopen station at 0.29 $\mu g/m^2$/day. Baker et al. (1994) measured atmospheric deposition of arsenic at three sites around the Chesapeake Bay over a 2 year period (Wye Research and Education Center site near Queenstown, MD; the Elms Site near St. Mary's City, MD; and the Haven Beach Site in Matthews County, VA) and found a long-term average bulk arsenic deposition rate of 0.37 $\mu g/m^2$/day. Collectively, these studies suggest an average long-term bulk arsenic atmospheric deposition rate on the order of 0.33 $\mu g/m^2$/day. Using this average deposition rate, the annual contribution of arsenic to Delmarva soils due to atmospheric deposition is 0.00043 mg/kg. This assumes topsoil (0-20 cm depth) with a mass of 2,800,000 kg/ha and density of 1.4 g/cm^3 as prescribed by Sparks et al. (2007). If accurate, the calculated soil arsenic concentration after one year due to atmospheric deposition would be 279 times less than the arsenic soil concentration of 0.12 mg/kg calculated by Sparks et al. (2007) following a year of poultry litter application.

The Wye Research and Education Center has had a number of biosolids samples analyzed over the last few years (Fisher et al., unpublished data). The total arsenic concentrations in these samples were generally lower than those found in poultry litter. Of four samples from a large sewage treatment plant in the Washington D.C. area analyzed for arsenic in 2008, three were non-detects (method detection limit (MDL) = 1.28 mg/kg) and one was 3.23 mg/kg, below the quantitation limit (QL) but above the MDL. A composted sample from this

same treatment plant had a total arsenic concentration of 6.2 mg/kg. Biosolids samples from two other major sewage treatment plants in Pennsylvania and Maryland had total arsenic levels of 8.67 and 4.25 mg/kg, respectively. It is interesting to note that when this Maryland biosolids sample was composted, the arsenic concentration increased to 10.5 mg/kg. In contrast to samples from sewage treatment plants from the western shore, a biosolids sample from a major Eastern Shore treatment plant collected in 2010 had an arsenic concentration of 24.1 mg/kg. It appears that, in general, biosolids contain less arsenic poultry litter where roxarsone is fed at prescribed amounts. However, there are notable exceptions suggesting that this area may require additional investigation. Some preliminary analyses of several biosolids and poultry litter samples also indicates that the proportion of water-extractible arsenic in biosolids is significantly less than that of poultry litter (Fisher et al., unpublished data). For example, recent analysis of 12 poultry litter samples with measurable total arsenic concentrations indicated that 65% (±9.0%) of total arsenic was water extractable while only 12% (±3.2%) of total arsenic in 3 biosolids samples was water extractable. This may be due to the amount of iron added to biosolids which will bind arsenic tightly. Again, this is preliminary data and further studies are required.

Although there currently are no regulations that apply directly to rates of arsenic applied to cropland in Maryland as a result of application of poultry litter, there are regulations that restrict arsenic application to cropland in biosolids (Code of Federal Regulations, 2011). The maximum arsenic concentration permissible for biosolids are not directly applicable to poultry litter since there is a maximum instantaneous concentrations limit (75 mg/kg), and a monthly average concentration limit (41 mg/kg) since many waste water treatment plants produce sludge on an ongoing basis. Although, a few arsenic concentrations values for poultry litter greater than 41 mg/kg have been reported as discussed in Question 1, generally this limit would not restrict application of most poultry litter to cropland. The other restriction on arsenic in biosolids regulations is the maximum cumulative loading rate which specifies that no more than a total of 41.4 kg/ha of arsenic may be applied to cropland as a result of repeated applications of biosolids. For poultry litter with an average arsenic content of 40 mg/kg, this would mean that total application allowed to any particular field would be 1035 Mg/ha (462 ton/acre). If there was no arsenic present in the soil initially and all applied arsenic remained in the top 30 cm of the soil profile, adding 41.4 kg/ha to this layer would raise the soil arsenic concentration to

approximately 10 mg/kg, very close to the DNREC soil arsenic standard of 11 mg/kg reported by Sparks et al. (2007). Applying poultry litter annually at rates to meet crop nitrogen (9 Mg/ha) and phosphorus (2 Mg/ha) requirements would mean that the cumulative loading rate limits for arsenic in current biosolids regulations would allow poultry litter applications every year for approximately 115 and 517 years, respectively. As discussed earlier in Question 3, these times would decrease substantially if the Maryland reference background of 3.6 mg/kg was used in these calculations rather than the Delaware standard.

(7) How are recent changes in phosphorus based nutrient management likely to change arsenic additions to Maryland cropland?

The accumulation of phosphorus (P) in agricultural soils in both Maryland and Delaware due to repeated applications of poultry litter is well documented (Coale, 2000; Sims, 2000). Since arsenic (As) is co-applied with phosphorus in poultry litter, changes in phosphorus management will result in changes in the application of arsenic to cropland. The value for arsenic excreted per bird calculated by Gabarino et al. (2003) and used by Sparks et al. (2007) was 42 mg/bird. Phosphorus excretion per bird prior to recent diet adjustments has been estimated to be approximately 14 gm for an average 2.3 kg broiler produced in Maryland (Staver and Brinsfield, 2001). This results in an average As:P ratio of approximately 0.003 on a mass basis. This is consistent with As:P ratios calculated based on reported poultry litter arsenic (40mg/kg, Sparks et al., 2007) and phosphorus (1.3 %, Codling et al., 2008) concentrations although reported ranges for both can vary widely depending on flock feeding and house management practices. The As:P ratio in poultry litter can be used to make estimates of past arsenic applications based on soil P concentrations and also how future changes in P applications will affect arsenic additions and accumulation in soil.

Although numerous studies have been conducted on plant available soil phosphorus levels in Maryland cropland, relatively little information exists on soil total phosphorus concentration. Codling et al. (2008) collected soil total phosphorus data from cropland and adjacent wooded areas from seven Maryland Eastern Shore farms with a history of poultry litter use. Total phosphorus concentrations for the top 30 cm of the soil ranged from approximately 600 to 1000 mg/kg higher in cropland as compared to adjacent wooded areas. Using the same bulk density assumption (1.4 g/cm^3) as Sparks et al. (2007), an increase in total phosphorus

concentration of 600 to 1000 mg/kg in the top 20 cm of the soil indicates a net addition of phosphorus to the soil of approximately 1680 to 2800 kg/ha. Using an As:P ratio of 0.003 yields an estimate of total arsenic added of from 5.0 to 8.4 kg/ha which would be sufficient to raise soil arsenic concentration approximately 1.8 to 3.0 mg/kg beyond background levels which Sparks et al. (2007) reported as 2.0 ppm for Delaware. This soil background level is very similar to measured levels in crop fields at the Wye Research and Education Center where there was no history of poultry litter application. Sparks et al. (2007) ran several scenarios assuming past poultry litter application practices and calculated increases in total soil arsenic concentration ranging from 3 to 5 mg/kg. Sims (2000) reported average annual phosphorus surpluses on a typical Delaware poultry farm of 61 kg/ha which would indicate that it would take from approximately 27 to 46 years to accumulate the total phosphorus levels reported by Codling et al. (2008) which supports Sparks et al. (2007) using 40 year scenarios to predict past arsenic accumulation in cropland soils.

In 1998, the Water Quality Improvement Act was passed in Maryland which made phosphorus based nutrient management mandatory on all cropland. While there are many details associated with phosphorus based nutrient management, in the long-term it will limit the buildup of soil phosphorus concentrations and therefore will restrict applications of phosphorus containing wastes such as poultry litter. After a transitional period, most soils will be managed so as to keep phosphorus concentrations relatively stable, meaning that phosphorus will only be added at a rate approximately equivalent to rates of removal in harvested crops. Coale (2000) reported typical phosphorus removal rates for grain crops of 17 to 26 kg/ha. If all phosphorus is supplied using poultry litter with the As:P ratio discussed earlier (0.003), an annual application of phosphorus of 25 kg/ha would result in an annual arsenic application of 75 gm/ha. Again using a soil bulk density value of 1.4 gm/cm^3 this would increase average soil arsenic concentrations in the top 20 cm by 0.027 mg/kg/year assuming no losses of arsenic. Approximately 37 years would be required for soil total arsenic to increase 1 mg/kg. To reduce the surplus of phosphorus in concentrated animal production systems, efforts have been made to reduce diet phosphorus levels and resulting phosphorus excretion. For broilers, reductions in phosphorus excretion of 30 to 40% seem to be achievable (Angel et al., 2005) and have been reported for commercial broiler production in Delaware (Hansen et al., 2005). Presumably this also has occurred in Maryland since the same companies operate in both states. If arsenic

feeding rates were kept the same, but phosphorus levels in broiler diets were cut so as to decrease the phosphorus content of poultry litter by 40%, the As:P ratio in poultry litter would increase to approximately 0.005. This would mean that supplying 25 kg/ha/yr of phosphorus with poultry litter would result in an annual arsenic application of approximately 120 gm/ha cutting the time required to increase soil arsenic concentrations by 1 mg/kg to approximately 23 years. Even under this scenario, the time required to raise soil arsenic concentrations to 11 mg/kg from the initial starting soil arsenic concentration assumed by Sparks et al. (2007) of 5 mg/kg would be approximately 140 years assuming no losses. The time to exceed the reference soil level would be much less than this if the Maryland soil background concentration of 3.6 mg/kg was used in the calculations. Overall, phosphorus based nutrient management would reduce rates of arsenic accumulation in fields where poultry litter was historically applied at rates well in excess of crop phosphorus needs, but reductions in phosphorus content of poultry litter without changes in diet arsenic content will increase the rate of soil arsenic accrual.

Phosphorus based nutrient management will tend to limit the applications of any waste material that previously was applied at rates that over applied phosphorus relative to crop needs. Another large phosphorus source in Maryland that has increased due to increasing population and increased efficiency of phosphorus removal from human waste streams is biosolids. Similar to the case for poultry litter, phosphorus based nutrient management will reduce biosolids application rates. Since As:P ratios in biosolids tend to be lower than historic levels in poultry litter, arsenic accumulation in soils will tend to be slower when using biosolids to meet crop phosphorus needs. However, as reported in Question 6, biosolids can be highly variable depending on the treatment system and incoming waste stream so a wide range in As:P ratios would be expected.

Although phosphorus based nutrient management will reduce rates of arsenic applications to particular fields, from a statewide perspective it will not affect the total amount of arsenic in poultry litter or the total amount of arsenic applied to Maryland cropland unless poultry litter is exported from the state. Phosphorus based nutrient management promotes greater spatial distribution of poultry litter applications to cropland formerly fertilized only with inorganic phosphorus fertilizer as poultry litter applications become restricted to reduce continued soil phosphorus buildup in concentrated poultry producing areas. Overall, phosphorus based nutrient

management will promote greater spatial distribution of the arsenic in poultry litter. A likely result will be that rates of arsenic application to fields in poultry producing regions will tend to be reduced but will actually increase in fields formerly fertilized only with inorganic phosphorus fertilizers but which now receive poultry litter applications as a consequence of restrictions on rates of poultry litter applications near production facilities.

8) How does arsenic behave in Coastal Plain soils?

Much like phosphorus, arsenic tends to have limited mobility in Coastal Plain soils. As described in Question 3, Rutherford et al. (2003) showed that arsenic in poultry litter is highly water soluble. This explains why surface applied poultry litter can result in elevated arsenic concentrations in surface runoff even though the amount of arsenic added to the soil was relatively small in comparison to the existing pool of arsenic in the top 20 cm soil layer. However, once arsenic comes into full contact with the soil, like phosphorus, it tends to bind to iron and aluminum oxides and clay minerals (Arai, 2010). This is why Rutherford et al. (2003) found the much larger pool of tightly bound soil arsenic to have much lesser effect on water soluble arsenic. Since phosphorus and arsenic behave similarly from a soil chemistry perspective, much can be learned about arsenic behavior from studies of phosphorus movement in Coastal Plain soils. In detailed studies of phosphorus sorption patterns in Delaware soils with histories of repeated poultry litter applications, Mozaffari and Sims (1994) found most crop land soils to have a high capacity to retain phosphorus, although there was a wide range in phosphorus binding capacity related to widely varying clay contents. The risk of downward movement of phosphorus was found to be greatest in coarse-textured soils, which would be expected to be the case for arsenic as well. But even in soils with relatively low iron and clay contents, most phosphorus remained bound in upper soil horizons. The limited mobility of arsenic in soils typically used for crop production on the Delmarva Peninsula is why Sparks et al. (2007) could predict with some certainty how future soil arsenic concentrations would change under varying application scenarios. The same budgeting approach also is applicable for phosphorus (Staver and Brinsfield, 2001) but not for soil constituents like nitrogen or sulfur which can leach readily, resulting in loss of a major fraction of added material to groundwater.

Despite the relative immobility of arsenic in soils containing clay and oxides of iron and aluminum, again, similar to the case for phosphorus, increasing overall arsenic concentrations

leads to some downward movement in the soil profile (Rutherford et al., 2003). Since arsenic and phosphorus both readily bind to iron and aluminum oxides, and since both are co-applied in poultry litter, there is some concern that high phosphorus content of poultry litter will increase the potential for arsenic leaching by competing for soil binding sites. Sparks et al. (2007) did extensive sorption and desorption experiments with phosphorus and arsenic and concluded that high phosphate concentrations in soil solution could lead to desorption of arsenic. But since subsoils tend to be relatively high in clay and iron and aluminum, there is a great capacity to retain both phosphorus and arsenic, preventing its movement into groundwater. If low oxygen conditions develop, the solubility of arsenic is increased (Arai, 2010). Most soils used for crop production, especially more coarse-textured soils, are generally well oxygenated. However, in settings where the water table is shallow and periodically rises into upper soil horizons, both phosphorus and arsenic movement in shallow storm flow would be expected to increase, although little detailed information on this process is available from studies in the Coastal Plain. Denver et al. (2004) reported dissolved arsenic in one groundwater sample in a surficial aquifer (6 ft. depth) in the south-central part of the Delmarva Peninsula and attributed detectable concentrations to recharging groundwater passing through organic-rich buried marine sediments, a situation that creates low oxygen conditions favorable for bringing bound arsenic into solution.

In summary, both Sparks et al. (2007) and Rutherford et al. (2003) indicated that arsenic in poultry litter is highly water soluble, creating potential for short-term losses with water moving across the soil where litter was surface applied, and movement downward through the soil profile immediately after poultry litter application. However, most soils have a high capacity for binding arsenic and most applied arsenic soon becomes unavailable for leaching. Despite most arsenic in surface soils being tightly bound, as surface soils become more enriched in arsenic, the potential for downward movement increases, but the movement is limited in most soils due to the high capacity for binding of arsenic to clay minerals and oxides of iron in aluminum in subsoil horizons.

Acknowledgements:

Table 1. Arsenic soil background remediation standards for Delaware and Maryland

State	Arsenic Background Remediation Concentration (mg/kg total As)
Delaware (DNREC, 2007)	11
Maryland (MDE, 2008)	3.6 (eastern MD)

Table 2. Arsenic water quality criteria for the protection of aquatic and human life

Regulating entity	Protection of Aquatic Life (µg/L as inorganic As(III))				Human Health Carcinogens (µg/L as inorganic As(III))	
	Fresh Acute Criteria	Fresh Chronic Criteria	Marine Acute Criteria	Marine Chronic Criteria	Fish ingestion[a]	Fish ingestion & water consuption[b]
Delaware (DNREC, 2004)	340	150	69	36	10	10
Maryland (MDE, 2011b)	340	150	69	36	1.4[c]	0.18[c]
U.S. EPA (USEPA, 2009)	340	150	69	36	0.14[d]	0.018[d]
Canada (µg/L total As) (CCME, 2001)[e]	5.0		12.5			

[a] Criteria in rivers and streams if waters are used for consumption of fish.
[b] Criteria in rivers and streams if waters are used both as drinking water and for consumption of fish (Since Maryland and Delaware only use groundwater for drinking water on the Delmarva Peninsula, these stream criteria are of limited applicability).
[c] Criterion based on carcinogenicity of 10^{-5} risk.
[d] Criterion based on carcinogenicity of 10^{-6} risk.
[e] Canadian arsenic water quality criteria provided for reference.

Table 3. Arsenic sediment criteria for Delaware, Maryland and the U.S. EPA – Region 3

State	Arsenic sediment criteria (mg/kg total As)
Delaware (DNREC, 1999)	8
Maryland (MDE, 2010)	70
U.S. EPA Region 3 (USEPA Region 3, 2011)	Freshwater – 9.8; Marine – 7.24

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