

Roxarsone in Natural Water Systems

R. L. Wershaw¹, J. R. Garbarino², and M. R. Burkhardt³

Organic arsenic compounds are extensively added to the feed of broiler chickens. The most commonly used arsenic compound is roxarsone (3-nitro-4-hydroxyphenylarsonic acid), which is fed to poultry to control coccidial intestinal parasites, thereby improving feed efficiency. Very little of the roxarsone is retained in the chicken meat (FDA limit is 0.5 parts per million in chicken muscle tissue). Most of the roxarsone is excreted unchanged; however, the degradation product, 3-amino-4-hydroxyphenylarsonic acid, has been detected in the urine of hens fed roxarsone. We estimate that approximately 10⁶ kilograms (Kg) per year of roxarsone and its degradation products are introduced annually into the environment from the disposal of poultry litter spread onto agricultural fields near the chicken houses. This practice could result in localized arsenic pollution.

No studies have been conducted on the fate of roxarsone or the degradation pathways of the compound in soils and natural waters. However, it is possible to predict the types of degradation reactions that roxarsone could undergo by consideration of the environmental behavior of compounds that contain one or more of the same structural units as roxarsone. Three of the most likely reactions are listed in Table 1.

Table 1. Possible environmental reaction mechanisms of roxarsone

Reaction	Examples
Reduction of nitro group	Reduction of trinitrotoluene in soil to monoamines and diamines.
Oxidative aromatic ring fission	Enzymatic oxidative fission of lignin units to form aliphatic acids.
Rupture of C-As bond	Conversion of organoarsenicals to arsenate by ultraviolet irradiation.

Microbial biodegradation of aromatic compounds takes place in the following sequence: N- and O- demethylation, hydroxylation, and deamination followed by ring fission, chain shortening, and oxidative removal of substituents. Oxidative ring fission leads to the formation of carboxylic acid groups on the cleaved ends of the rings. If roxarsone were to undergo such a reaction sequence, arsonoalkyl acids would be produced. The arsonoalkyl acids could then undergo conversion to alkylarsines, which are stable under anaerobic conditions. Under aerobic conditions, methylarsines undergo rapid oxidation to AsO₄³⁻. The degradation reactions outlined above indicate that 3-amino-4-hydroxyphenylarsonic acid, methylarsines, and AsO₄³⁻ are possible environmental-degradation products of roxarsone. In order to assess the environmental impact of introduction of large amounts of roxarsone into a watershed, the concentrations of each of these compounds must be measured in the soils, sediments, and natural waters of the watershed at different times during the hydrologic cycle.

The U.S. Geological Survey will develop separate analytical methods to measure roxarsone and its organic and inorganic degradation products in surface water, ground water, and soils. Inorganic arsenic species currently are determined by using ion chromatography to separate the species followed by hydride generation and inductively coupled plasma-mass spectrometric detection. Detection limits are 0.2 microgram per liter (µg/L) for arsenate and arsenite using a 100-microliter (µL) injection. Organoarsenic compounds, including roxarsone and 3-amino-4-hydroxyphenylarsonic acid, will be separated using reverse phase liquid chromatography and determined by electrospray mass spectrometry. We anticipate a detection limit for roxarsone of 50 nanograms per liter (ng/L) using a 50-µL injection. Surface- and ground-water samples will be processed in the field to separate the inorganic and organic species using a polymeric solid phase extraction cartridge. Organoarsenic compounds will be extracted from the cartridge with 0.2% trifluoroacetic acid in acetone. Roxarsone and its metabolites will be extracted from soils using methylene chloride prior to analysis by electrospray mass spectrometry.

¹U.S. Geological Survey, Box 25046, MS 408, Denver Federal Center, Denver, CO 80225-0046 (rwershaw@usgs.gov)

²U.S. Geological Survey, Box 25046, MS 407, Denver Federal Center, Denver, CO 80225-0046 (jrgarb@usgs.gov)

³U.S. Geological Survey, Box 25046, MS 407, Denver Federal Center, Denver, CO 80225-0046 (mrburk@usgs.gov)