UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION 10
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Reply to: OEA-095
Attn of: grepo-grove.gina@epa.gov

MEMORANDUM

Subject: QA Narrative Report for the Analysis of Veterinary Pharmaceuticals in Lagoon, Soils, Water and Waste Water Samples Collected from the Phase 3 Yakima Valley Nitrates Study by University of Nebraska Lincoln – Water Science Laboratory

From: Ginna Grepo-Grove, R10 QA Manager
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To: Michael Cox, Project Officer, OEA
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CC: Stephen R Hutchins, TOPO, USEPA, NRMRL

The quality assurance (QA) review of the analytical data generated from the analysis of 63 samples collected from the above referenced site has been completed. These samples were analyzed for the following veterinary pharmaceutical products: chlortetracycline, erythromycin, lincomycin, monensin, oxyteracycline, ractopamine, sulfachloropyridazine, sulfadimethoxine, sulfamerazine, sulfamethazine, sulfamethazole, sulfamethoxazole, sulfathiazole, tetracycline, tiamulin, tylosin and viriginamycin following the University of Nebraska Water Science Laboratory located in Lincoln, NE (UNL's) in-house Standard Operating Procedure (SOP.

The following samples were evaluated in this validation report:

Lagoon Samples

LG01	LG02	LG03	LG04	LG05	LG06
LG07	LG08	LG09	LG10	LG11	LG12
LG13	LG14	LG15			

Water Samples

WW-01	WW-02	WW-03	WW-04	WW-05	WW-06
WW-07	WW-08	WW-09	WW-10	WW-11	WW-12
WW-13	WW-14	WW-15	WW-16	WW-17	WW-18
WW-19	WW-20	WW-21	WW-22	WW-23	WW-24

WW-25	WW-26	WW-27	WW-28	WW29	

Soil/Solid Samples

S0-01	SO-02	SO-03	SO-04	SO-05	SO-06
SO-07	SO-08	SO-09	SO-10	SO-11	SO12
SO13	SO14	SO15	SO-16		

Waste Treatment Plant (WWTP) Samples

SP01	SP02	SP03

DATA QUALIFICATIONS

All sample analyses were evaluated following the EPA's Stage 2B Manual Data Validation Process (S2VM). The analyses were evaluated and laboratory qualifiers were mapped to R10 EPA validation qualifiers following the technical acceptance criteria and Quality Control Specifications outlined in the UNL SOP specified above and the Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use (EPA-540-R08-005).

Limitations of the Data Validation:

The following documents were used as supporting documentation for data review:

- *QA Report UNL June 2011*
- *Vet Pharm Instrument Calibration Report 09212010*
- *Vet Pharm Instrument Calibration Report 09282010*
- *Vet Pharm Instrument Calibration Report 10082010*
- *Vet Pharm Instrument Calibration Report 10222010*
- *Vet Pharm Instrument Calibration Report 11162010*
- *Vet Pharm Calibration Report 04142011*
- *Vet Pharm Calibration Report 04182011*
- *Vet Pharm Calibration Report 04191011*
- *Vet Pharm Calibration Report 04212011*
- *Vet Pharm Calibration Report 04222011*
- *Vet Pharm Calibration Report 04252011*
- *Vet Pharm Calibration Report 04272011*
- *Vet Pharm Sequence 2010-2011- Internal Standard Report*
- *Summary of Sample Analytical Results*

The conclusions presented herein are based on the information provided for the review. None of the detected results and calculations were verified using the instrument raw data.

Overall Assessment: Except for those analytes qualified unusable, the rest of the veterinary pharmaceuticals data, as qualified, are usable. Due to the complexity of the liquid matrices (water, lagoon and WWTP) and chromatographic interferences, internal standards used for calculating the concentrations of the target compounds were affected resulting in a potentially high biased associated data. Data users are warned to use the reported values with caution as the concentrations of the compounds in the samples maybe lower than what were reported.

Approximately 9% of the total data points were qualified unusable and additional 18% were qualified estimated concentration with a high bias due to out of control internal standards and or calibration. Five Lincomycin and 3 monensin results in the water samples were detected above the reporting limits but were flagged non-detects due to contamination in the associated field blank, WW29.

DISCUSSION:

Holding Times: Holding times were met by all samples. All of the samples were stored frozen at -20C after receipt at the lab.

Soil/Sediment Samples:

Sixteen soil/sediment samples were processed and analyzed following the using microwave assisted solvent extraction (MASE), followed by LC/MS/MS of extracts according to *"Analysis of Steroids in solid samples (i.e. soils, manure, etc) by microwave-assisted solvent extraction (MASE) and liquid chromatography-tandem mass spectrometry (LC/MS/MS)"* (SOP# Analyte-Steroids_Solids-001).

QC results (Analysis Date: 11/11/2010):

Duplicate Results: Sample SO-04 was analyzed in duplicate. Duplicate Results were acceptable and none of the target vet pharmaceuticals were detected in both runs.

Matrix Spike Results: Sample SO-12 was used for matrix spike analysis. Recoveries were acceptable and ranged from 72% - 131%. No solid/sediment data were qualified on this basis.

Laboratory Fortified Blank (LFB) Results: The frequency of analysis and the recovery results of LFB are acceptable. Recoveries ranged from 56% -131%. No solid/sediment data were qualified on this basis.

Blanks: The target compounds were not detected in any of the reagent blanks associated with the samples analyzed. None of the solid/sediment results were qualified on the basis of contamination in the blank(s).

Water, Lagoon and Waste Water Treatment Plant (WWTP) Samples

Due to the complexity of the sample matrices, multiple analyses (up to 5 runs per sample including dilutions) were performed utilizing UNL SOPs with varying modifications on sample and extract clean-up techniques. The calibration standards also went through the clean-up processes with the samples. Initial calibration runs were analyzed before each analytical sequence. For the final report, the validator reported the sample runs with better analytical QC results and least affected by the matrix as indicated by the internal standard recoveries and calibration results.

Analytical Method 1: The liquid samples were processed and analyzed following the SOP "*Analysis of veterinary pharmaceuticals in water samples using a Spark Holland symbiosis on-line C18 cartridge solid phase extraction (SPE) and high pressure liquid chromatography/tandem mass spectrometry (HPLC/MS/MS)*"; Document File number: LCMS_VET_PHARM_WATER_001; Issue Effective Date: 12/2010 – Present. This SOP was utilized for liquid samples analyzed in 2010.

Analytical Method 1 with Modified Cleanup Technique: The liquid samples were processed and analyzed following the SOP "*Analysis of veterinary pharmaceuticals in water samples using a Spark Holland symbiosis on-line C18 cartridge solid phase extraction (SPE) with 500 uL of 2.4 M Citric Acid Solution and high pressure liquid chromatography/tandem mass spectrometry (HPLC/MS/MS)*"; Document File number: LCMS_VET_PHARM_WATER_002; Issue Effective Date: 2/2011 – Present. This SOP was utilized for liquid samples analyzed in 2011

Data Qualifiers

The following is a list of validation qualifiers applied to the sample result(s) when needed to indicate an associated out-of-control QA/QC results.

Data Qualifiers		
	U	The analyte was not detected at or above the reported result.
	J	The analyte was positively identified. The associated numerical result is an estimate.
	UJ	The analyte was not detected at or above the reported estimated result. The associated numerical value is an estimate of the quantitation limit of the analyte in this sample.
	R	The data are unusable for all purposes.
	N	There is evidence the analyte is present in this sample.
	JN	There is evidence that the analyte is present. The associated numerical result is an estimate.