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**Study #245: Dissipation of simazine and diuron from surface and sub-surface depths
in a leaching vulnerable California soil**

I. Introduction

As part of DPR's registration process, the Environmental Monitoring Branch (EM) evaluates the potential of new pesticide active ingredients that exceed the specific numerical values (Johnson, 1989) to move to ground water based on their predicted behavior in the environment. One tool used in the evaluation process is the LEACHM pesticide fate model developed by Hutson and Wagenet (1992), coupled to a probabilistic procedure to provide estimates of the amount of pesticide residues that are leached from simulated agricultural applications (Troiano and Clayton, 2004). These estimates are compared to known California ground water contaminants obtained by model simulations of similar hypothetical applications. The modeling scenario used for these pesticide evaluations is a commercial grape production operation on a Fresno County irrigated sandy-loam textured soil, where ground water contamination by pesticides has frequently occurred. These soils have been shown to be vulnerable to pesticide leaching under irrigated conditions (Troiano et al., 1993). Spurlock (2000) determined the hydraulic properties of this soil required by LEACHM using bromide tracer movement reported by Troiano et al. (1993).

An estimate of the pesticide's soil half-life rate constant is an important physical-chemical parameter required by LEACHM. As observed from previous EM evaluations, the output from LEACHM can vary by an order of magnitude or more in response to the half-life rate constants available, which are currently determined from terrestrial field dissipation (TFD) studies. In these studies residues of the compound rarely move below a depth of 30 cm because water applications seldom provide for significant percolation. In contrast, our modeling scenario predicts pesticide movement and dissipation throughout a 3-m deep soil profile, which includes the rooting depth of a mature grape crop. For lack of available data, EM applies half-life rate constants derived from TFD studies (<30 cm depth) to the entire soil profile being modeled. However, several studies demonstrate that the dissipation rate typically decreases significantly with depth (Frank and Sirons, 1985; Johnson and Lavy, 1994; Kruger et al., 1993), often correlating with decreasing biomass (Kordel et al, 1995; Miller et al., 1997). Our simulated Fresno County soil has been well characterized by Troiano et al. (1993), revealing that the organic matter content declines from 1.2 % at the surface to 0.5 % at 30 cm deep and to 0.2 % at 45 cm deep.

Atrazine and its metabolites were reported to degrade more rapidly in subsurface, low organic-matter, fully saturated soils than in the same unsaturated soil. However, these degradation rates were still considerably longer than in unsaturated layers near the soil surface that were higher in organic matter (Kruger et al., 1993). These findings indicate that hydrolytic reactions are a significant atrazine dissipation process in subsurface, well-hydrated or -irrigated soils, but are not the primary dissipation process in presence of organic matter. Others also have suggested that chemical processes such as hydrolysis are the dominant pesticide degradation pathways in sterilized soils or those largely void of organic matter (Miller et al., 1997). EM's current modeling techniques may overestimate pesticide degradation rates because half-life rate constants derived from organic-matter containing soils are applied to subsurface soil layers void of organic matter. This scenario would underestimate the potential for ground water contamination by pesticides.

EM scientists currently use a LEACHM model input file that consists of a 20-layer soil horizon totaling 3 m in depth. Depth-specific values are assigned to soil textural properties, soil bulk density, organic carbon content, initial plant root distribution, and initial soil volumetric water content. Other depth-specific values can be optionally calculated by the model or are treated as dynamic variables after initially assigned constant values such as Campbell's water retention parameters and initial soil temperature, respectively. However, for lack of information, incorporation of depth-specific half-life rate constants into the input file has not been possible.

This study will provide data that will enable the recalibration of the LEACHM input file with depth-specific half-life rate constants. The hypothesis is that for this soil type, chemical hydrolytic processes rather than biotic degradation dominate pesticide dissipation once residues are moved to soil layers very low in organic matter. Soil movement of herbicides in profile will be established using two levels of water application. Persistence and mobility data will be used to calibrate LEACHM by setting the shallowest soil layers to reported and/or observed degradation rates and the lower-most layer to the reported hydrolytic half-life rate adjusted to the observed soil temperature. Using an iterative numerical optimization process, half-life rate constants will be determined for the remaining soil horizons. Comparisons amongst the two water treatments will provide confirmation of the derived soil distribution of half-lives.

II. Study Objective

The objective of this study is to establish depth-specific half-life rate constants for simazine, its degradates ACET and DACT, and diuron throughout the simulated soil profile, and use this data set to recalibrate the LEACHM pesticide fate model.

III. Personnel

Study personnel from the Environmental Monitoring Branch of DPR include:

Project Leader: Murray Clayton

Field Coordinators: Cindy Garretson and Alfredo DaSilva
Senior Scientist: John Troiano
Project Supervisor: Lisa Quagliaroli
Laboratory Liaison: Carrisa Ganapathy for analyses conducted by CDFA
Cindy Garretson for analyses conducted in Fresno
Cooperators: David Zoldoske, California Water Institute (CWI), CSU
Fresno
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IV. Study Design

This study will be conducted on bare ground plots established at California State University, Fresno. A non-replicated, randomized, split-plot design will be used. Two treatment plots will each be treated with simazine and diuron at maximum label rates of 5.4 kg a.i./ha (4.8 lb a.i./acre) and 3.6 kg a.i./ha (3.2 lb a.i./acre), respectively. Bromide will also be applied at 84 kg/ha (75 lb/ac) as a conservative tracer for the movement of water.

Prior to solute application, EM will determine background pesticide concentrations, soil texture, organic carbon content, and bulk density from a randomly selected split-plot within each irrigation treatment plot (Figure 1). Within 72 hours prior to pesticide application, additional soil cores will be obtained from the same split-plot to determine soil gravimetric water content. Simazine, diuron and bromide will be applied to the soil by chemigation using micro sprinklers during the primary irrigation event to transport the materials to their target depths. The two levels of percolating water will establish the center-of-mass of the pesticides at two depths: near the soil surface for one plot and at approximately 1.5 m below the surface for the second plot. Soil temperature buffering will contrast between these depths (Figure 2) and potentially influence degradation processes. The primary irrigation event will be conducted in late June or early July to reflect the maximum expected contrast in mean soil temperature between the targeted soil depths (Figure 3). Actual water application rates will be determined by LEACHM, which will be indexed to measured ETo rates (CIMIS weather station #80 at California State University, Fresno), soil characterization, and measured soil gravimetric water content from the plots.

Twenty-four hours following the irrigation event, soil sampling to 3 m will be initiated in a randomly selected split-plot within each irrigation treatment plot (Figure 1) to confirm actual mass of solute applied and establish the initial distribution of the solute through the soil profile. After a 45 – 50 day incubation period that may include minor supplemental irrigation events to maintain soil hydration, final soil sampling in the remaining split-plot of each irrigation treatment plot (Figure 1) will be conducted to a depth of 3 m.

In the study by Troiano et al. (1993), the application of a bromide tracer and three levels of water treatment provided insight into water movement through the soil. Hydrological variables in LEACHM were successfully calibrated with this data (Spurlock, 2000).

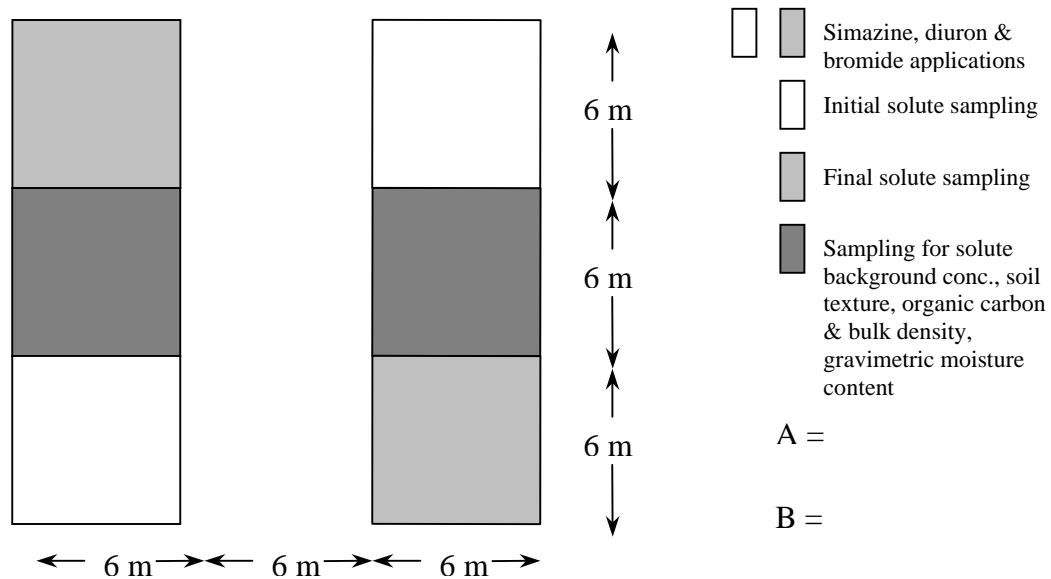


Figure 2. Diurnal temperature variation of a Chilean soil at several depths (Sakamoto, 2001).

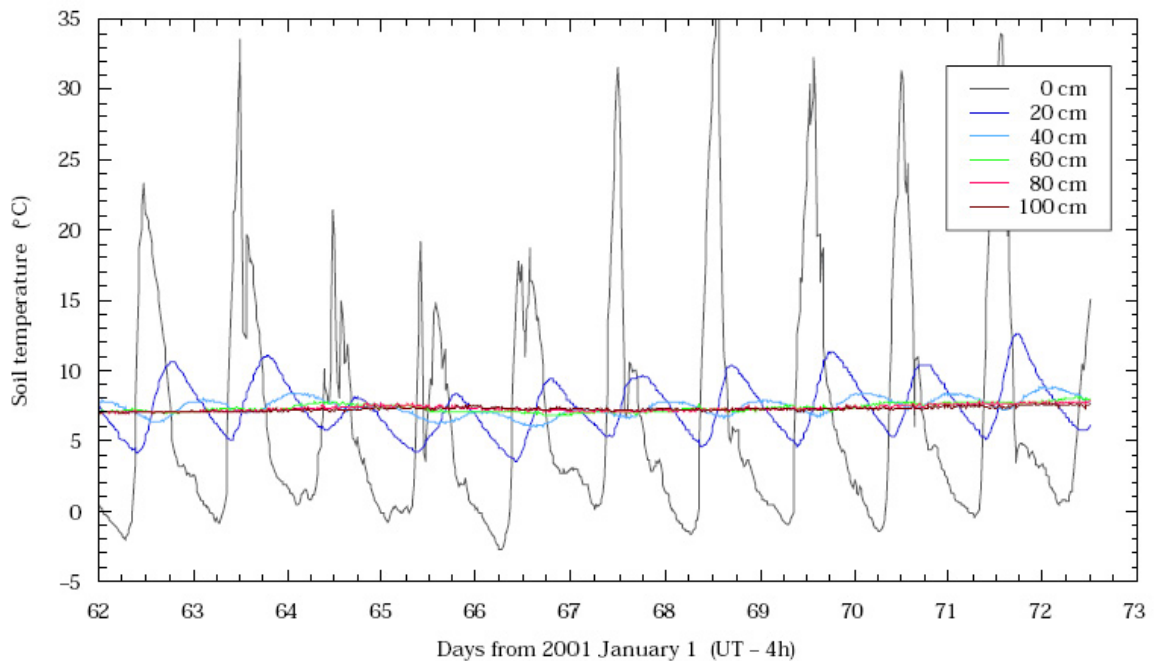
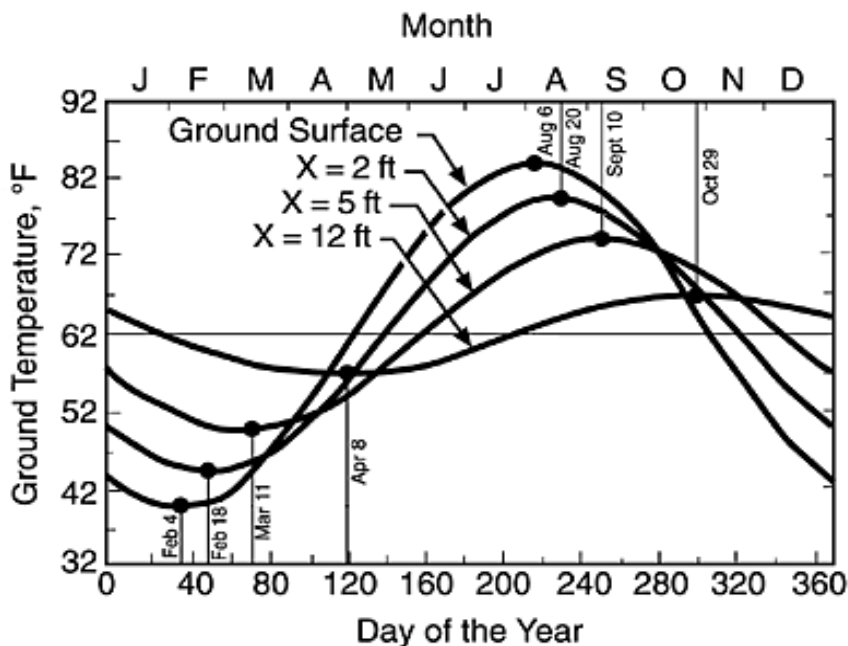


Figure 3. Seasonal soil temperature as a function of depth below ground surface for an average moist soil in coastal Virginia (US Dept. of Energy).



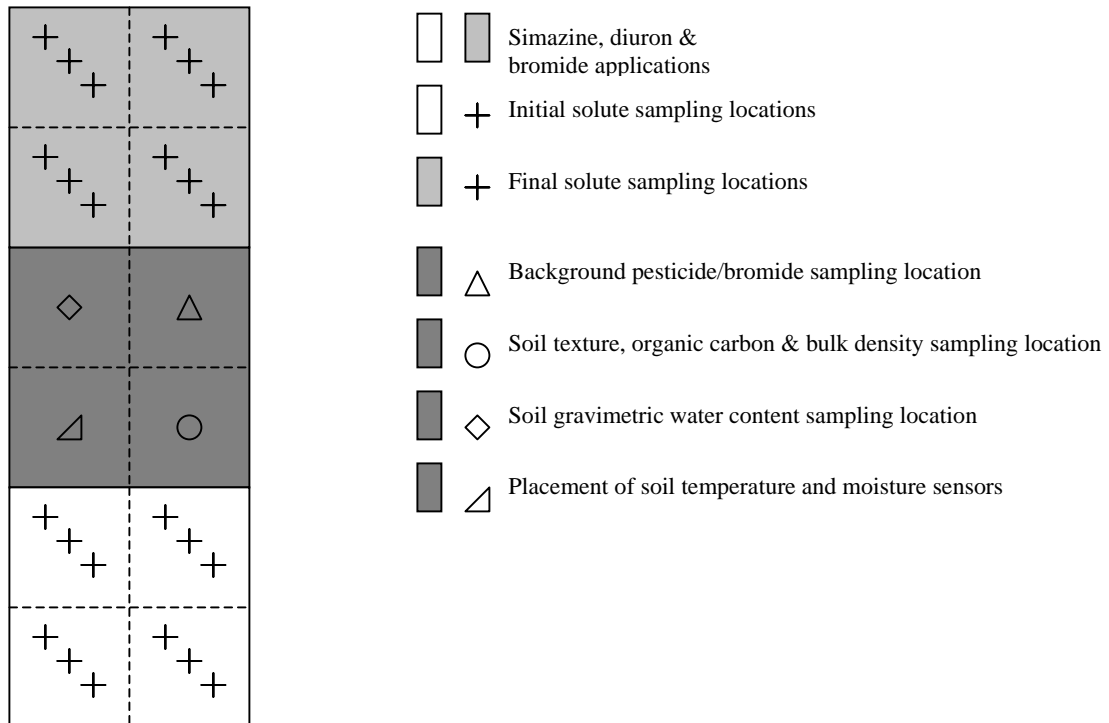
V. Sampling Methods

Establishing background pesticide concentrations will consist of obtaining a soil core from the center of a randomly selected quadrant within the designated split-plot of each irrigation treatment (Figure 4). The cores of 3-m depth will be partitioned into 300 mm long samples for analysis of background pesticide and bromide concentrations. An additional core sampled around this time, also at the center of a randomly selected quadrant within the same split-plot of each irrigation treatment will characterize soil texture, organic carbon and bulk density in 150-mm deep increments (Figure 4), which corresponds to the LEACHM-simulated soil layer depths. Immediately preceding solute application, soil gravimetric water content will be determined from a 3-m core segregated into at 150-mm deep increments in a randomly selected quadrant as previously described (Figure 4). In the remaining quadrant, sensors will be incorporated into the soil profile to electronically log soil temperature and soil moisture content to a depth of 3 m at 150-mm deep increments for the duration of the field experiment (Figure 4).

The chemigation and irrigation treatments will then be conducted using micro sprinklers. Soil coring will begin 24 h after completion of the irrigation treatments. Three cores will be sampled along a diagonal transect located within each quadrant of the designated initial split-plot (Figure 4). Soil samples will be collected in 150 mm long segments to a depth of 3 m. Soil segments of corresponding depths within each quadrant will be combined and homogenized producing four replicate, depth-specific, composite soil cores per irrigation treatment. Soil coring will alternate between quadrants of the irrigation treatment plots thereby creating a “blocking” effect for the 2- or 3-day period that soil sampling will take. Samples will be frozen until chemical analysis is conducted.

Final soil sampling for pesticide residues and bromide will be conducted 45-50 days from solute application. Procedures for this sampling event will be consistent with those of the initial sampling event with the exception that the soil cores will be obtained from a separate split-plot (Figure 4). Samples will be frozen for later chemical analysis.

Figure 4. Representative irrigation treatment with split-plots segregated into sampling quadrants.



Sampling will be conducted according to the following DPR standard operating procedures (SOP):

SOP FSSO001.00 for soil bulk density determination (Garretson, 1999a).

SOP FSSO002.00 for soil sampling, including auger and surface soil procedures (Garretson, 1999b).

SOP METH001.00 for soil water content (Garretson, 1999c).

SOP METH005.00 for organic carbon content (Gunasekara, 2006).

VI. Chemical Analysis and Quality Control

The CDFA Center for Analytical Chemistry has developed analytical methods for determining simazine and its metabolites ACET and DACT, and diuron concentrations in soil. Pesticide residue and bromide analyses are to be conducted on 299 or 376 soil

samples, depending on the depth of solute testing in the low water application treatment (Table 1). Soil cores to the full 3-m depth will be collected and stored from this treatment plot but chemical analysis to 1.5 m may be sufficient if solute movement is prevented below 1.5 m deep.

Twenty samples will be collected for residue background concentrations, 120 or 160 samples to confirm solute mass application and to determine initial solute distribution in the soil, 120 or 160 samples to determine final soil solute distribution and concentrations, and 39 or 52 samples for QA/QC (Table 1). For QA/QC field sampling, approximately 5% of the total samples collected will consist of submitting split-replicated samples. Approximately 10% of total samples collected will be needed for laboratory QA/QC purposes, consistent with SOP QAQC001.00 (Segawa, 1995). CWI personnel will conduct analyses to determine bromide concentrations and pH of the soil samples.

Table 1. Sample numbers to be analyzed.

Sampling event	Irrigation treatments		Sub-total		
	Low water application		High water application	Low count	High count
	Low count	High count			
Background	10 ^z	10 ^z	10 ^z	20	20
Initial	40 ^y	80 ^x	80 ^x	120	160
Final	40 ^y	80 ^x	80 ^x	120	160
QA/QC field split reps	4	8	8	12	16
QA/QC lab spikes	9	18	18	27	36
Sub-total	103	196	196		
Grand total				299	376

^zNumber of samples from a 3-m deep core segmented into 300 mm sections (1 core x 10 sections).

^yNumber of samples from a 1.5-m deep core segmented into 150 mm sections (4 composite cores x 10 sections).

^xNumber of samples from a 3-m deep core segmented into 150 mm sections (4 composite cores x 20 sections).

VII. Data Analysis

LEACHM uses Campbell's equation to describe the relationship between soil water matric potential and soil water content. With existing estimates of these hydraulic parameters predicted bromide and water movement through the soil profile will be compared to bromide tracer data from the initial and final sampling events and soil moisture data from field sensors for the two levels of irrigation treatment. If the field data is in relative agreement with predicted data the site-specific hydraulic parameters of soil water matric potential, soil water content, and dispersivity will be re-estimated for the field site using the bromide tracer recovery data and the LEACHM model with an optimization procedure described by Spurlock et al. (2006). Success of the optimization procedure will reflect an improvement in the minimization of sum of squares between predicted and measured bromide concentrations across both irrigation treatments for the re-estimated hydraulic parameters.

LEACHM-predicted movement of the pesticide residues using depth-constant, half-life rate data, will be compared to measured concentrations from the field for both levels of irrigation treatment. Relative agreement between measured and predicted concentrations for the two levels of irrigation treatment will confirm the suitability of the measured data for further analysis. Simazine and diuron concentration and depth data from the field study will then be used in a second optimization procedure using LEACHM and the computer program PEST (Watermark Computing, 1998). The PEST program will manage an iteration process of LEACHM runs to provide best-fit estimates of depth-specific half-life rate constants for each pesticide. The half-life rate constants in the surface layers will be fixed during the optimization procedure based on the calculated half-life of the pesticides from the low water application treatment. Reported hydrolytic half-life data for the pesticides will fix half-life rate constants at the deepest soil layers using measured soil temperatures to select or calculate their appropriate rates. The optimization process will utilize linear and non-linear mathematical functions to establish best-fit estimates of half-life rate constants for the remaining soil layers. If chemical hydrolysis fails to adequately characterize degradation rates in the lowest soil layers then further optimization procedures will be conducted to produce empirical estimates of the changing rate of degradation with soil depth. Success of the optimization procedures will reveal improved minimization of sum of squares between predicted and measured residue concentrations across both irrigation treatments.

LEACHM has the capabilities to model the transformation and environmental fate of metabolites from their parent products. The measured simazine metabolites ACET and DACT will provide a dataset from which future plans to model these transformations will enable further model development possibilities.

VIII. Timetable

Approximate date	Order of activity	Responsibility of study activity
Prior to June, 2007	Determination of study location and plot configuration	CWI & DPR Fresno
Prior to June, 2007	Preparation of treatment plots (surface preparation, weed control, etc)	CWI
Prior to June, 2007	Determination of soil textural properties and organic matter content	DPR Fresno
Early June, 2007	Soil coring for background pesticide concentrations and preparation of samples for cold storage	CWI & DPR Fresno & DPR Sacramento
Early June, 2007	Transportation of soil samples to Sacramento	DPR Sacramento
Early June, 2007	Establishment of water application equipment	CWI
Early June, 2007	Establishment and testing of soil temperature and soil moisture content sensors	CWI
June 22, 2007	Commencement of soil temperature and soil moisture content monitoring	CWI
June 23-25, 2007	Soil coring to determine soil gravimetric water content	DPR Fresno
June 26, 2007	Determination of water application treatment rates to the plots using LEACHM (based on measured soil textural properties and soil gravimetric water content)	DPR Sacramento
June 27, 2007	Chemigation of pesticides and bromide to treatment plots during primary irrigation event	CWI
June 28-30, 2007	Soil coring to confirm solute mass application and establish initial solute distribution in the soil profile and preparation of samples for cold storage	CWI & DPR Fresno & DPR Sacramento
June 30, 2007	Transportation of soil samples to Sacramento	DPR Sacramento
June 30 - Aug 13, 2007	Maintenance irrigation to preserve soil hydration in solute containing soil horizons (based on ET and data from soil moisture sensors and/or LEACHM)	CWI
June 26 - Aug 14, 2007	Collection of weather data (CIMIS data from CSUF site)	CWI
Aug 13-15, 2007	Soil coring to establish final solute distribution in the soil profile and preparation of samples for cold storage	CWI & DPR Fresno & DPR Sacramento
Aug 15, 2007	Transportation of soil samples to Sacramento	DPR Sacramento
Aug - Oct, 2007	Analysis of soil cores for bromide concentration	CWI
Aug - Oct, 2007	Analysis of soil cores for simazine and its metabolites ACET and DACT, and diuron	CDFA
Nov 2007 - May 2008	Data analysis, reporting and publication of results	CWI & DPR Fresno & DPR Sacramento

IX. Budget

Budget component	Units		Expense/unit (\$)	Total component expense (\$)	
	Low	High		Low	High
CWI	1	1	99,235	99,235	99,235
Pesticide sample analysis	299	376	500	149,500	188,000
Equipment & supplies	1	1	5,000	5,000	5,000
Travel	1	1	2,000	2,000	2,000
PY	0.5	0.5	100,000	50,000	50,000
Total				305,735	344,235

X. References

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