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AMBIENT AND LANDFILL-IMPACTED GROUNDWATER QUALITY IN THE HUDSON VALLEY OF SOUTHEASTERN NEW YORK STATE

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ABSTRACT

A large amount of groundwater quality monitoring data has been collected in connection with solid waste landfills regulated by the New York State Department of Environmental Conservation. Although sampling personnel and analytical laboratories are different for each site, a high degree of uniformity in methods is assured by state regulations which govern environmental monitoring at the landfills. In this study, data for selected parameters was pooled from upgradient, presumably uncontaminated, monitoring wells installed in different rock formations at a large number of sites in order to characterize regional variability in ambient groundwater quality. Parameters selected for this study are those considered to be most useful in detecting landfill-derived groundwater contamination and include alkalinity, ammonia, arsenic, chloride, chemical oxygen demand, hardness, iron, manganese, total phenols and total dissolved solids. Comparisons are made with data from monitoring wells downgradient of the landfills and with other available data sets. Emphasis is placed on whether parameters exceed applicable water quality standards in ambient groundwater and whether the parameters selected are reliable indicators of landfill-derived groundwater contamination. This study should be particularly useful in cases where topography, property boundaries or other site constraints make it impossible to site a valid upgradient monitoring point or where groundwater quality impact assessments must be made using a single monitoring point.

Keywords: alkalinity, ammonia, arsenic, chloride, COD, hardness, iron, manganese, phenols, TDS, solid waste, landfill

1. INTRODUCTION

In evaluation of groundwater quality impacts from landfills or other contamination sources, it is always preferable to obtain site-specific upgradient or background water quality data for comparison with results obtained from a downgradient groundwater monitoring well. This is not always possible. There are cases where, due to the location of a monitored facility relative to

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[§] This research was carried out by staff at the New York State Department of Environmental Conservation. Views and conclusions presented herein are those of the authors and do not represent official Department policy. Address correspondence to Steven Parisio, New York State Department of Environmental Conservation, 21 South Putt Corners Road, New Paltz, NY, USA, 12561, 845-256-3126, sxparisi@gw.dec.state.ny.us groundwater flow divides, property boundaries or physical constraints, it may not be possible to install a monitoring well outside of the zone of potential facility-related groundwater contamination. In other cases, it may be necessary to evaluate potential water quality impact based on results from a single monitoring point such as a residential water supply well which may be close to an unmonitored landfill or other contamination source. In such cases, it would be helpful to have a numerical value which represents the upper threshold of ambient groundwater quality for a given parameter within the region.

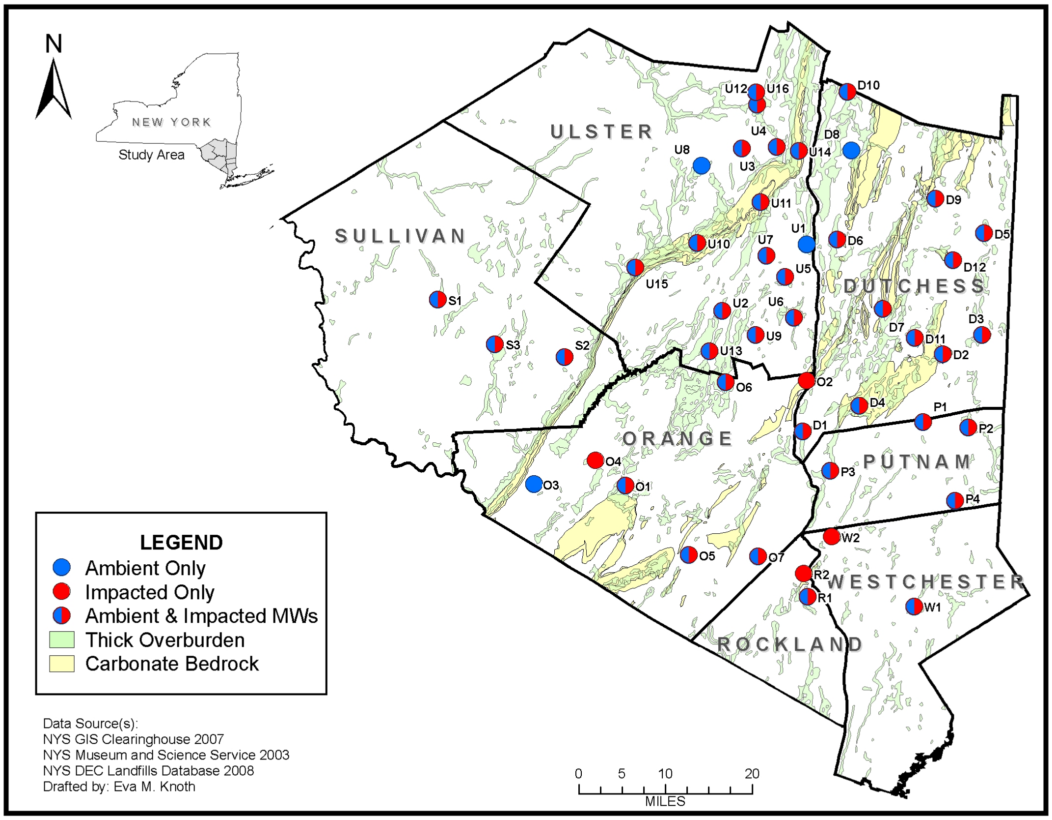
New York State's 6 NYCRR Part 360 Solid Waste Management Facilities Regulations require that operators of solid waste landfills install groundwater monitoring wells upgradient (where possible) and downgradient of the facility, sample the wells one or more times each year, and analyze the samples for a suite of parameters which include leachate indicators (e.g. alkalinity, hardness, COD), inorganic parameters (e.g., iron, manganese, chloride) and volatile organic compounds. The data generated is routinely used to characterize groundwater quality impacts or evaluate effectiveness of remedial measures at individual sites. Prior to this study, there has not been an effort to compile upgradient water quality monitoring data from multiple landfill sites and to use the pooled data to characterize ambient groundwater quality or define its variability on a regional basis.

1.1 Study Area

The data were compiled from groundwater monitoring reports submitted in connection with inactive solid waste landfills which are regulated by the New York State Department of Environmental Conservation. As shown in figure 1, the study area consists of seven counties within the Hudson Valley Region of southeastern New York State, corresponding to the geographic area which is administered by the Department's Region 3 Office, headquartered in New Paltz, New York. The counties included are Westchester, Putnam, Dutchess, Rockland, Orange, Ulster and Sullivan.

1.2 Previous Studies

Previously published data sources which can be used to characterize groundwater quality within the study area include a series of water supply reports for individual counties prepared by the United States Geological Survey in cooperation with various governmental agencies or commissions in New York State (Asselstine and Grossman 1955, Frimpter 1970, Grossman 1957, Perlmutter 1959, Soren 1961, Simmons et al. 1961). Data from these county water supply reports along with other similar historical data sources can also be found in USGS reports which summarize water quality data for New York State (Heath 1964) or for the Hudson River Basin (Hammond et al. 1978). These reports are of significant historical interest but may not provide an entirely adequate basis for characterizing current conditions with respect to ambient groundwater quality within the region. Limitations and problems associated with use of this historic data include a rather short list of parameters, a lack of information regarding the specific analytical methods used to generate the data and the use of sample collection points which were designed and constructed for water supply rather than groundwater quality monitoring purposes. Unlike the groundwater monitoring wells used to generate the contemporary data compiled for the present study, the water supply wells and springs used to generate the data presented in the historical water supply reports would generally have been designed and constructed in a manner which would not prevent infiltration of surface water, chemical interactions with well construction materials or mixing of groundwater from several discrete aquifer segments or water bearing zones.



Data Source(s):
NYS GIS Clearinghouse 2007
NYS Museum and Science Service 2003
NYS DEC Landfills Database 2008
Drafted by: Eva M. Knoth

Figure 1. Study area showing landfill sites, county boundaries and selected, generalized geologic mapping units. Geologic mapping units are shown only to give an indication of their regional distribution and are not intended to provide geologic information relative to individual sites. Areas not shaded are underlain by non-carbonate bedrock with relatively thin overburden.

2. MATERIALS AND METHODS

2.1 Selection of monitoring points

A total of 46 landfills with regular groundwater quality monitoring programs were selected for inclusion in this study. Data from upgradient groundwater monitoring wells at 42 of the sites were used to compile the ambient groundwater quality data set, referred to henceforth as the "ambient data set". Four of the 46 sites were not included in the ambient data set because they do not have an upgradient groundwater monitoring well. Data from downgradient groundwater monitoring wells at 42 sites was used to compile the landfill-impacted groundwater quality data set, henceforth referred to as the "impacted data set". At all of the sites included in the impacted data set, the predominant waste type disposed of in the landfills was municipal solid waste (MSW). Four of the 46 sites which have waste types other than MSW were excluded from the impacted data set to eliminate variability with respect to the type of water quality impact being evaluated. The locations of sites which are included in the ambient set, impacted data set, or both data sets, are shown in Figure 1. Summary information regarding the composition of the ambient and impacted data sets is provided in Table 1.

Table 1. Composition of Data Sets with Respect to Site & Well Characteristics

Site & Well Characteristics		**Ambient data set**	**Impacted data set**
Total number of sites included in data set		42	42
General site location	Dutchess County	12	11
	Orange County	5	6
	Putnam County	4	4
	Rockland County	1	2
	Sullivan County	3	3
	Ulster County	16	14
	Westchester County	1	2
Landfill waste type	Municipal solid waste	38	42
	Other waste types	4	0
Monitoring well position	Upgradient	42	0
	Downgradient	0	42
Monitored aquifer type	Overburden	20	30
	Carbonate rock	6	2
	Non-carbonate rock	16	10

Data included in both the ambient and landfill-impacted data sets was collected over a time frame extending, roughly, from 1990 to 2007. For the purposes of this study, temporal trends which may exist in the data, especially in the landfill-impacted data set, were not considered. Such temporal trends are beyond the scope of this study and will be considered in a later study focusing on post-closure trends in groundwater quality downgradient of the landfills.

All of the landfills included in this study had at least three downgradient monitoring wells to choose from and many of the sites had more than one upgradient or background monitoring well. In selecting upgradient monitoring wells for inclusion in the ambient data set, an effort was made to minimize the potential for landfill-derived groundwater quality impact or impacts from other significant contaminant sources. Preference was given to wells completed in bedrock, wells screened at deeper levels in the aquifer, and wells located as far upslope of the landfill boundary as possible. In selecting downgradient monitoring wells for inclusion in the impacted data set, an effort was made to capture the full extent of landfill-derived groundwater quality impact. Here, preference was given to shallow wells located directly downgradient from the thickest portions of the landfill. As shown in Table 1, use of these preferences resulted in a higher proportion of bedrock monitoring wells in the ambient data set (22 of 42) and a lower proportion of bedrock wells in the landfill-impacted data set (12 of 42). Regardless of what preferences are used, a lower proportion of bedrock wells downgradient of the facilities is unavoidable because of the natural tendency for unconsolidated deposits to thicken in the down slope direction due to the typical geometry of glacial deposits such as kames, valley-fill outwash sands and gravels, or glaciolacustrine silts and clays.

2.2 Parameters selected for evaluation

New York State's Part 360 regulations require landfill operators to sample groundwater at landfills four times per year except where case-specific approval is granted for a reduced sampling frequency. Twenty one "routine parameters" are analyzed during all quarterly sampling events and an additional 19 inorganic parameters and 47 volatile organic compounds are analyzed during annual "baseline" sampling events. At most of the sites included in this study, the sampling frequency was initially quarterly and was subsequently reduced to one baseline sampling event per year.

The ten parameters selected for this study are ammonia, alkalinity, arsenic, chloride, chemical oxygen demand (COD), hardness, iron, manganese, total phenols and total dissolved solids (TDS). These parameters were chosen because they are strongly associated with leachate or leachate-impacted groundwater, are frequently detected in downgradient monitoring wells and/or frequently exceed applicable water quality standards or guidance values. With the exception of arsenic, all are routine parameters which were analyzed initially at a quarterly frequency. With the exception of phenols, all of the parameters selected are detected more than 50% of the time in landfill-impacted groundwater monitoring wells.

2.3 Data compilation, data quality screening and preliminary evaluation

Data for the ten parameters of interest were extracted from monitoring reports submitted on behalf of the landfill operators by analytical laboratories or environmental consulting firms after each individual sampling event. In order to complete this "data-mining" effort, more than 1000 individual monitoring reports had to be reviewed. The data from all upgradient monitoring wells were combined in Microsoft Excel to create a single pooled data set to characterize ambient groundwater quality for each of the ten parameters. In cases where a parameter was analyzed but not detected, the laboratory reporting limit was recorded along with the "U" data qualifier. The same approach was used to create the impacted data set using pooled data from all of the downgradient monitoring wells. A third data set, referred to as the "historical ambient" data set was compiled using water quality data which was available for six of the parameters (alkalinity, hardness, TDS, chloride, iron and manganese) in published water supply reports for Dutchess, Putnam, Rockland, Sullivan, Orange and Ulster counties.

To ensure that data used for statistical calculations would meet basic standards for quality and usability, a limited data quality evaluation was performed. All detected values in each of the pooled data sets were retained but a portion of the non-detects were discarded based on review of the associated laboratory reporting limits (RLs) in relation to contract required quantitation limits (CRQLs) or alternative criteria. In the case of the historic ambient data set, a small amount of non-detect data was discarded in cases where the data was reported as a zero value with no associated laboratory RL.

When dealing with non-detects, it is important to remember that the RL associated with the non-detect is not a function of actual groundwater quality. Rather, it is a function of the precision, or lack of precision, associated with the laboratory analysis (Helsel 2005). In reality, the RL represents the top of a range of possible values which might correspond to the actual parameter concentration in groundwater. The number or percentage of non-detects in a data set tells us something about water quality but the usefulness of this information is greatly reduced when the RLs associated with the non-detects are elevated relative to the applicable water quality standard and/or typical detected values within the same data set.

Non-detects were not present in the data sets for alkalinity, chloride, hardness and TDS. In the case of arsenic, phenols, iron and manganese, non-detect data was discarded if the RLs exceeded the contract required quantitation limit (CRQL) as specified in the Department of Environmental Conservation's Analytical Services Protocol (NYSDEC 2000). In the case of ammonia and COD, very few of the non-detects had RLs low enough to satisfy the applicable CRQLs and alternative screening criteria were needed to avoid drastic reductions in the size of the data sets. For these two parameters, non-detect data were only discarded in cases where the associated RLs exceeded the median concentration for detected values within the ambient data set.

Prior to selecting methods for statistical comparisons and graphing, a determination had to be made regarding whether the data sets were likely to follow a normal Gaussian distribution. Four of the data sets (ammonia, arsenic, COD and phenols) contained a high percentage of non-detects and were therefore not suited for evaluations using parametric statistics which require that an absolute value, rather than just a relative value or rank, be known for each of the data points. For the remaining six parameters (alkalinity, chloride, hardness, iron, manganese and TDS), means, standard deviations and coefficients of variation were calculated and, with the exception of one parameter (alkalinity), coefficients of variation were greater than 1.0 indicating that the data were not normally distributed. To further evaluate whether the data were normally distributed, skewness, kurtosis, and the D'Agostino-Pearson Omnibus tests were used in accordance with widely accepted guidance for evaluation of groundwater quality data (EPA 1998). All of these tests confirmed that the data were not normally distributed and would best be evaluated using non-parametric tests and graphing methods as discussed below.

2.4 Summary statistics and graphing methods

For all parameters, non-parametric summary statistics including the median (50th percentile) and the 10th, 25th, 75th and 90th percentiles were calculated. In calculating these statistics, non-detects were assigned a numeric value equal to the associated laboratory RL (i.e., the highest potential concentration which could have been present in the sample). In the case of iron and manganese, where non-detects make up only a small percentage of the data sets, even though the non-detects were assigned the highest possible numeric values, they were still ranked below the 10th percentile and had no effect on the calculated values for the summary statistics or the appearance of diagrams constructed using the summary statistics. For these two parameters, and four parameters without any non-detects (alkalinity, hardness, chloride and TDS), truncated box and whisker diagrams showing the 10th percentile, 25th percentile, median, 75th percentile and the 90th percentile of each data set were plotted in accordance with standard practices (ASTM 1995).

In the case of ammonia, arsenic, COD and total phenols, non-detects were more numerous and the highest potential concentrations for some of the non-detects were higher than the median or, in some cases, the 75th percentile for the data set. As a result, it was not possible to calculate 10th percentiles, medians or 75th percentiles without introducing uncertainty due to the need to assign an arbitrary numeric value to the non-detects. For these parameters, statistics describing the lower portions of the distribution were omitted from the tables and frequency histograms were used to graph the data in lieu of box and whisker plots.

The non-parametric Mann-Whitney t-test was used to make comparisons between historical and contemporary ambient groundwater quality data sets and between ambient and landfill-impacted data sets. This test was only used for the six parameters which have few or no non-detects and which are covered by both the contemporary and historical ambient data sets. For the purposes of this test, as recommended by Helsel (2005), all non-detects were ranked as equal and assigned a numeric value equivalent to the highest RL in the data set.

3. RESULTS AND DISCUSSION

Summary statistics for the contemporary (1990-2007) ambient groundwater quality data set are provided in Tables 2a and 2b. Variability within the contemporary ambient data set due to aquifer type is illustrated in Figures 2a and 2b. Table 3 provides summary statistics for the historical (1937-1960) ambient groundwater quality data set along with results of a statistical comparison between the historical and contemporary data sets. Tables 4a and 4b provide summary statistics for the landfill-impacted groundwater quality data set and a statistical comparison between the ambient and impacted data sets.

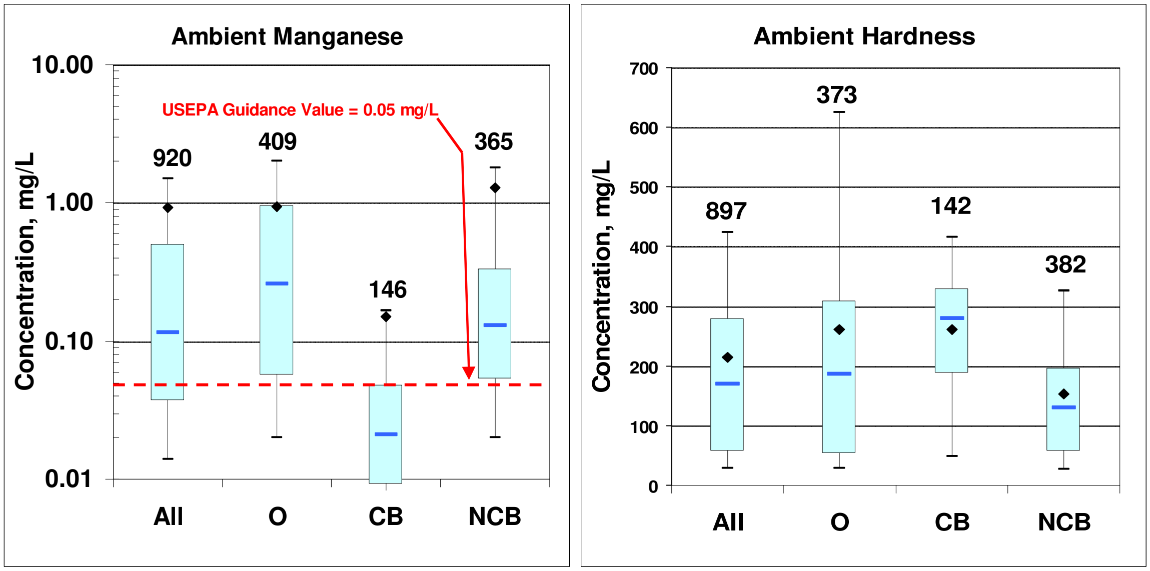
Graphs comparing the various data sets are provided in Figures 3a through 3f and 4a through 4d. A discussion of overall variability in the data sets and significant findings with respect to the ten parameters is provided below.

3.1 General sources of variability

Variability is expected to be present in both data sets due to differences in lithology as well as differences in the many drilling contractors, hydrogeologic consulting firms and analytical laboratories used to generate the data at the different landfill sites. A factor which tends to limit this variability is the need for all facility operators to comply with State regulations which prescribe detailed requirements for all aspects of groundwater quality monitoring including monitoring well location, design and construction, well development, sample collection and handling, laboratory analytical methods and quality assurance/quality control (QA/QC). Department staff review water quality monitoring work plans and provide oversight as needed to ensure that applicable regulatory standards are consistently adhered to. Analytical methods used generally conform to those prescribed in the New York State Department of Environmental Conservation's Analytical Services Protocol (NYSDEC 2000) and the U.S. Environmental Protection Agency's (SW-846) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods.

3.2 Variability attributable to differences in aquifer types

A certain amount of bias may have been introduced unavoidably due to differences in aquifer type between the wells included in the study. For the purpose of this discussion, aquifer types are divided into three basic categories: overburden, carbonate bedrock and non-carbonate bedrock. As discussed earlier, the proportion of monitoring wells screened in overburden is higher in the impacted data set than in the ambient data set and, to the extent that groundwater chemistry is different in overburden aquifers than in bedrock aquifers, this bias towards overburden wells may have affected the ambient vs. landfill-impacted water quality comparisons. As shown in Figures 2a and 2b, the differences are not large, but hardness tends to be highest in carbonate bedrock and lowest in non-carbonate bedrock aquifers with overburden aquifers falling in between. In the case of manganese, concentrations are lowest in carbonate bedrock and highest in overburden, with non-carbonate bedrock aquifers falling in between. These differences are not unexpected, since the availability of calcium and magnesium would be highest in carbonate rocks and the solubility of metals such as manganese would be lowest in the relatively alkaline pH associated with carbonate-rich environments. Overburden would also be expected to have a higher concentration of most dissolved constituents relative to non-carbonate bedrock due to the higher degree of weathering and the greater surface area available for interactions between solid and liquid phases. For both parameters, differences between bedrock and overburden aquifers are most pronounced in the case of carbonate bedrock which affects a relatively small percentage of the samples in either of the data sets.



Figures 2a and 2b. Box and whisker diagrams showing variability attributable to aquifer type within the ambient hardness and ambient manganese data sets. (Abbreviations: O = overburden, CB = carbonate bedrock, NCB = non-carbonate bedrock) The light blue box encloses the 25th to 75th percentiles of the data set. The median is represented by the blue horizontal bar, while the mean is represented by the black diamond. The upper and lower whiskers indicate the 90th and 10th percentiles, respectively. The number above each plot is the number of samples. Applicable groundwater quality standards or guidance values are shown as a dashed red horizontal line.

3.3 Ambient groundwater quality in relation to standards and guidance values

For each of the ten parameters studied, the 90th percentile of the ambient data set is suggested as an upper threshold value or screening level which can be used to define ambient groundwater quality for the region and to identify results which are indicative of groundwater quality impact from municipal solid waste landfills or other anthropogenic contamination sources. These values are presented along with other summary statistics in Tables 2a and 2b.

Seven of the ten parameters evaluated have applicable levels of concern such as promulgated federal and/or State groundwater quality standards, guidance values or maximum contaminant levels for drinking water. Of these, iron and manganese are the parameters which most frequently exceed the applicable level of concern. Iron exceeded its groundwater quality standard (0.3 mg/L) in 75% of the ambient groundwater quality samples. The iron standard is based on aesthetic considerations such as taste and color rather than health effects. Manganese exceeded the USEPA's health-based guidance value (0.05 mg/L) in 65% of the samples, making this the parameter of greatest potential concern from a public health standpoint. Like iron, manganese has traditionally been viewed as being primarily an aesthetic issue, but there are now an increasing number of studies indicating that manganese may have a number of adverse effects on human health (WHO 2004, ATSDR 2000).

Numerous regional studies have shown that ambient concentrations of arsenic in groundwater may exceed the EPA's maximum contaminant level (MCL) for drinking water (0.01 mg/L). In addition to the most well known areas in Bangladesh and West Bengal, India, elevated arsenic has been documented in a number of regions throughout the world including China, Vietnam, Hungary/Romania, Argentina, Chile, the southwestern USA and Mexico (Smedley and Kinniburg 2002). Areas where elevated arsenic concentrations have been reported in the eastern USA include New England (Ayotte et al. 2003), New Hampshire (Peters et al. 2006), Pennsylvania (Peters and Burkert 2008) and New Jersey (Serfes 2004), Results of this study show that southeastern New York State can be added the list with 11.5% of samples exceeding the MCL and a 90th percentile arsenic concentration of 0.013 mg/L in ambient groundwater.

Total phenols is another parameter with a health-based State groundwater quality standard (0.001 mg/L) which was frequently exceeded (27 percent) in samples in the ambient groundwater quality data set. The significance of these results is difficult to interpret because the analytical method used does not distinguish between non-toxic and naturally occurring phenols such as tannins, lignin breakdown products or other plant-related sources and toxic industrial chemicals such as phenol, cresols or pentachlorophenol. Experience with water quality monitoring programs has shown that total phenols often occur in groundwater which does not show any other landfill leachate indicators or other signs of anthropogenic contamination.

In addition to iron, manganese, arsenic and total phenols, total dissolved solids is a parameter which has a 90th percentile concentration above its applicable State groundwater quality standard (500 mg/L). For these five parameters, concentrations above the applicable standard fall within the range of variability which is representative of ambient groundwater quality for the region and concentrations exceeding the standard cannot be used as a sole basis to conclude that groundwater has been impacted by a contamination source.

3.4 Comparison of contemporary and historical ambient groundwater quality data

Comparison of Table 2a with Table 3, and inspection of Figures 3a through 3f show clear differences in ambient groundwater quality between the contemporary and historical data sets. For all six parameters, median concentrations are higher in the contemporary data sets than in the historical data sets. Mann-Whitney t-tests show significant differences in data sets for all six parameters with "p" values in all cases less than 0.001. By comparing the ratios of the medians, it is clear that these differences are much more pronounced in the case of iron and manganese than for the other parameters.

Table 2a. Ambient (Contemporary) Groundwater Quality Data Set – Summary Statistics
Parameters which are always or nearly always detected
Concentrations expressed in mg/L

Statistic	Alkalinity	Chloride	Hardness	Iron	Manganese	TDS
Count	912	922	897	947	921	907
# Non-detects	0	0	0	31	34	0
% Non-detects	0	0	0	3	4	0
Minimum	2	0.02	0.27	0.005	0.001	5
10th Percentile	24	1.4	29	0.1	0.014	69
25th Percentile	71	2.8	57	0.3	0.037	118
Median	142	6.6	170	1.2	0.12	233
75th Percentile	227	26	280	5.5	0.5	322
90th Percentile	316	78	424	19	1.5	526
Maximum	800	1140	3400	872	40.6	6012
Mean	163.9	38.93	214.5	11.2	0.92	287
Standard Deviation	128.7	98.01	248.9	47.7	2.96	314
Coefficient of Variation	0.8	2.5	1.2	4.3	3.2	1.1
Level of Concern	None	250	None	0.3	0.05	500
% Exceeding Level of Concern	NA	4.6	NS	75	65	11

Table 2b. Ambient (Contemporary) Groundwater Quality Data Set – Summary Statistics
Parameters which are frequently undetected
Concentrations expressed in mg/L

<table>
<tr><th>Statistic</th><th>Ammonia</th><th>Arsenic</th><th>COD</th><th>Phenols</th></tr>
<tr><td>Count</td><td>492</td><td>468</td><td>764</td><td>706</td></tr>
<tr><td># Non-detects</td><td>206</td><td>312</td><td>424</td><td>509</td></tr>
<tr><td>% Non-detects</td><td>42</td><td>67</td><td>55</td><td>72</td></tr>
<tr><td>Minimum</td><td colspan="4" rowspan="4">Values undefined due to uncertainties caused by non-detects</td></tr>
<tr><td>10th Percentile</td></tr>
<tr><td>25th Percentile</td></tr>
<tr><td>Median</td></tr>
<tr><td>75th Percentile</td><td>0.11</td><td colspan="3"></td></tr>
<tr><td>90th Percentile</td><td>0.6</td><td>0.013</td><td>38</td><td>0.015</td></tr>
<tr><td>Maximum</td><td>3.1</td><td>0.29</td><td>776</td><td>1.2</td></tr>
<tr><td>Contract Required Quantitation Limit (CRQL)</td><td>0.05</td><td>0.01</td><td>1.0</td><td>0.01</td></tr>
<tr><td>% of Non-detects exceeding CRQL</td><td>57</td><td>0</td><td>100</td><td>0</td></tr>
<tr><td>Level of Concern</td><td>2</td><td>0.01</td><td>None</td><td>0.001</td></tr>
<tr><td>% Exceeding Level of Concern</td><td>0.6</td><td>11.5</td><td>NA</td><td>27</td></tr>
</table>

Table 3. Summary Statistics - Historical (1937-1960) Ambient Data Set
All concentrations expressed in mg/L

Statistic	Alkalinity	Chloride	Hardness	Iron	Manganese	TDS
Count	278	486	510	403	105	291
Minimum	4	0.2	2	0	0.01	27
10th Percentile	19	1.6	36	0.02	0.01	82
25th Percentile	40	2.4	62	0.05	0.01	138
Median	71	4.2	116	0.11	0.01	198
75th Percentile	104	9	160	0.29	0.03	255
90th Percentile	143	15	220	0.59	0.1	322
Maximum	399	480	1100	4.60	2.5	1470
Mean	79	9.2	122	0.28	0.08	214
Standard Deviation	56	29	90	0.50	0.27	141
Coefficient of Variation	0.71	3	0.74	1.79	3.60	0.66
Level of Concern	None	250	None	0.3	0.05	500
% Exceeding Level of Concern	NA	0.4	NA	21	14	2.4
Comparative Statistics: Contemporary (1990-2007) Data Set vs. Historical Data Set						
Mann-Whitney p value	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	0.0006
Ratio of Medians, Contemporary to Historical	2	1.6	1.5	11	12	1.2
Ratio of 90th Percentiles, Contemporary to Historical	2.2	5.2	1.9	32	15	1.6

Iron and manganese are both parameters which exhibit redox-controlled solubility. The differences between historical and contemporary data for these two parameters are most likely attributable to a difference in sample preparation and turbidity. Although no information regarding analytical methods is provided in the water supply reports from which the historical data set was derived, a number of references can be cited to show that it would have been standard practice during the time period when the historical data was generated for researchers to filter groundwater samples prior to analysis for metals (Fishman and Downs 1966, Fishman 1993, Hem 1985). In more recent times, the practice of field filtering has been largely abandoned due to extensive experience acquired through environmental monitoring programs which has shown that filtration of samples prior to metals analysis using traditional methods such as the 0.45 micron membrane filter can lead to aeration of anoxic groundwater samples resulting in precipitation and loss of dissolved iron and manganese as well as mobile colloidal phases (Puls and Powell 1992, Puls and Barcelona 1989). Because field filtering is not permitted in New York State regulations pertaining to groundwater quality monitoring at solid waste landfills, the contemporary monitoring data is not directly comparable to the historical data derived from filtered samples. Further, it is believed that the historical data underestimates the actual concentration of iron and manganese which is representative of ambient groundwater quality for the study area and that the higher values reported for the contemporary data set are more representative of true ambient groundwater quality.

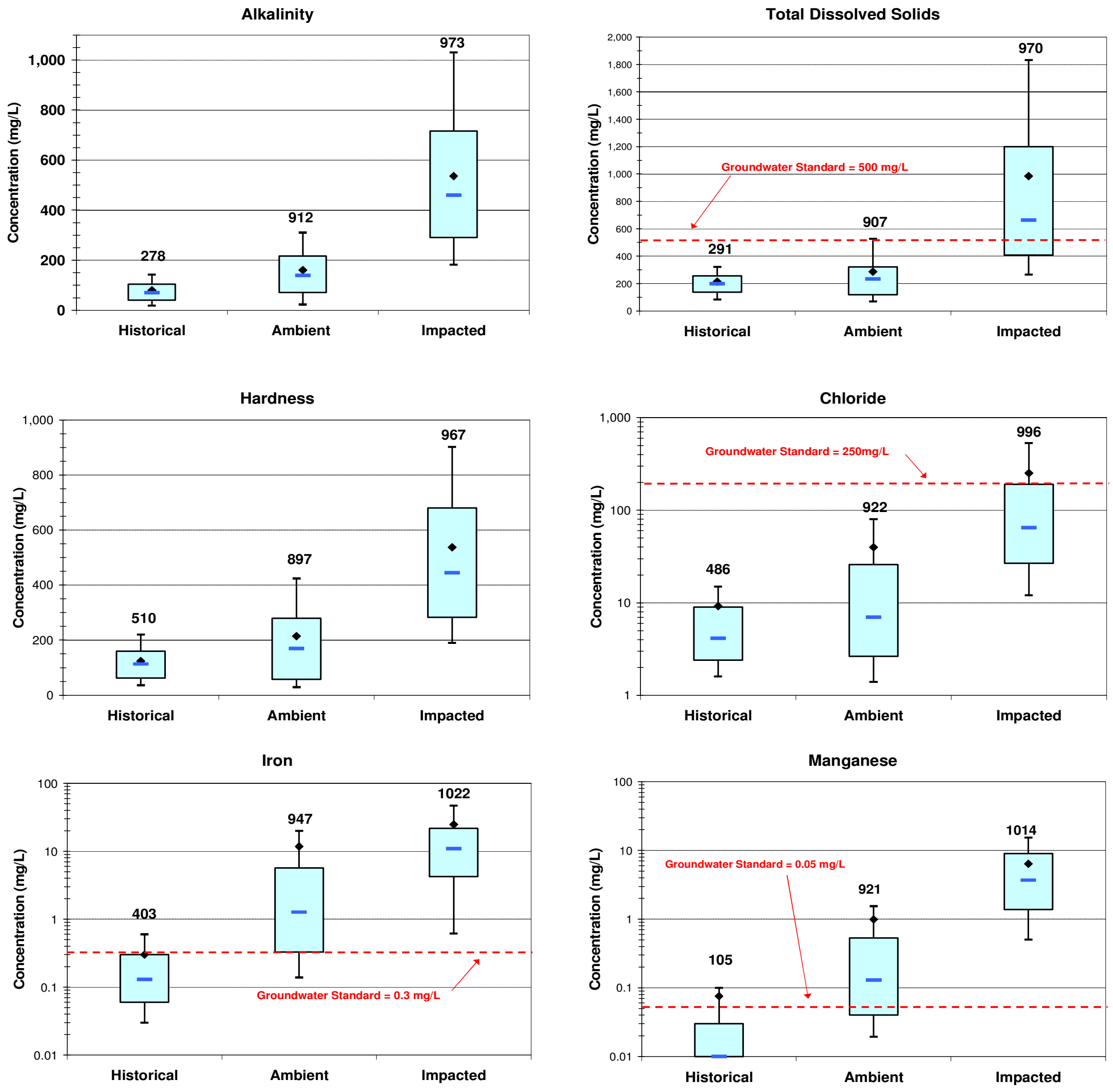
When a comparison of the 90th percentiles of the contemporary and historical data sets is made, chloride, like iron and manganese, stands out from the other parameters as being higher in the contemporary data set. This apparent increase in ambient chloride levels may be related in part to an increase in the amount of highway de-icing salt used now throughout the region as compared to what was used in the past. This affect is not expected to be large, however, because most of the upgradient monitoring wells used in the study do not receive recharge from areas potentially impacted by road runoff.

3.5 Comparisons of ambient and landfill-impacted groundwater quality

Differences between ambient groundwater quality and landfill-impacted groundwater quality are apparent by reviewing summary statistics (tables 2a, 2b, 4a and b) and graphs (figures 3a-f and 4a-d) for each of the ten parameters. To facilitate comparisons, the ratio of the impacted median concentration (I-50) to the ambient 90th percentile concentration (A-90) concentration was calculated for each parameter. In cases where the I-50/A-90 ratio is greater than one (alkalinity, hardness, total dissolved solids, manganese and ammonia), the parameter is considered to be a reliable indicator or landfill-derived groundwater quality impact. To determine the relative degree of usefulness of the parameters in distinguishing ambient from impacted groundwater quality, the I-50/A-90 ratios were ranked. Based on this ranking exercise, the relative degree of reliability for use in identifying landfill-derived groundwater contamination was determined to be as follows: ammonia > manganese > alkalinity > TDS > hardness > chloride > COD > arsenic > iron. In the case of phenols, a ratio could not calculated due to the high percentage of non-detects in both the ambient and impacted data sets, making this the least useful parameter for this purpose.

If the 90th percentile of the ambient data set is viewed as the threshold value for likely groundwater impact, the percent of samples in the impacted data set which exceeds this threshold can also be viewed as a measure of a parameter's usefulness in distinguishing between ambient from impacted groundwater quality. As in the case of the I-50/A-90 ratios, the percentage of impacted samples above the A-90 values can be ranked to determine the relative usefulness of parameters. Ranking of the >A-90 percentages yielded the following result with respect to relative usefulness of parameters: ammonia > manganese > alkalinity > TDS > hardness > chloride > arsenic > COD > iron > phenols. As in the previous exercise, the order of usefulness is similar, with ammonia, manganese and alkalinity being the three most useful contamination indicators and iron and phenols being the two least useful.

The relatively high ranks for ammonia and alkalinity as contamination indicators are not surprising because these are prominent constituents of landfill leachate which are related to the microbial decomposition of organic wastes within the landfill and are relatively mobile in groundwater. Iron and manganese are both naturally occurring, abundant and ubiquitous constituents of aquifers which can be mobilized by the reducing conditions in landfill leachate plumes but may also be elevated in ambient groundwater. Based on the results of this study, manganese must be given greater weight than iron as an indicator of landfill-derived groundwater quality impact.



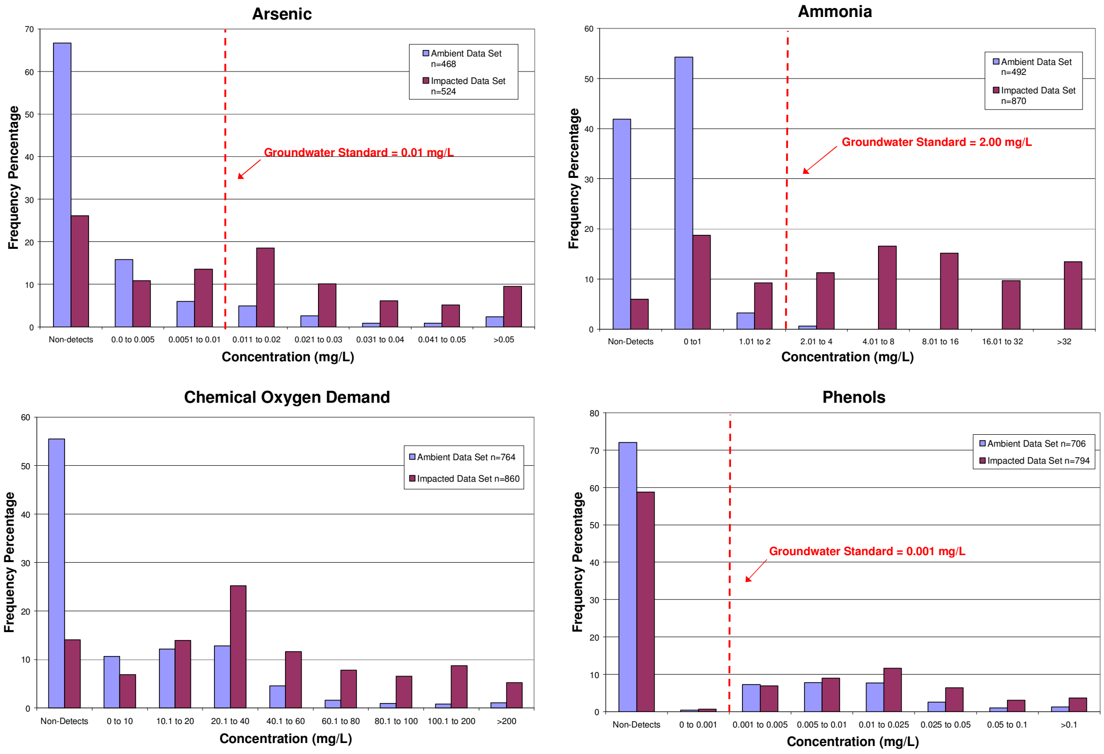
Figures 3a- 3f. Box and whisker diagrams illustrating differences between ambient/contemporary, ambient/historical and impacted data sets for six parameters with relatively few non-detects. The light blue box encloses the 25th to 75th percentiles. The median is represented by the blue horizontal bar and the mean is represented by the black diamond. The upper and lower whiskers indicate the 90th and 10th percentiles, respectively. The number above each plot is the number of samples. Applicable groundwater quality standards or guidance values are shown as a dashed red horizontal line.

Table 4a. Summary Statistics – Landfill-impacted Groundwater Quality Data Set
Parameters which are always or nearly always detected
Concentrations expressed in mg/L

Statistic	Alkalinity	Chloride	Hardness	Iron	Manganese	TDS
Count	973	996	967	1022	1014	970
# Non-detects	3	0	0	9	0	0
% Non-Detects	0.3	0	0	0.9	0	0
Minimum	1	0.094	0.12	0.0022	0.0005	2.60
10th Percentile	182	12.1	190	0.62	0.50	265
25th Percentile	290	27	283	4.2	1.4	408
Median	460	65	445	11	3.7	663
75th Percentile	716	191	681	22	9.0	1200
90th Percentile	1030	532	902	47	15	1831
Maximum	5370	7270	7212	1330	81	9920
Mean	535	252	537	25	6.3	984
Standard Deviation	363	619.7	480.4	77	7.9	1109
Coefficient of Variation	0.68	2.46	0.89	3.10	1.2	1.13
Level of Concern	None	250	None	0.3	0.05	500
% Exceeding Level of Concern	NA	21	NA	93	98	65
Comparative Statistics – Ambient vs. Impacted Data Sets						
Impacted 50/Ambient 90 Percentile	1.46	0.83	1.05	0.58	2.47	1.26
Ratios Ranked	8	4	6	2	9	7
% Impacted Values > Ambient 90th P	70	44	56	29	73	62
% Impacted > Ambient 90th P Ranked	8	5	6	2	9	7

Table 4b. Summary Statistics – Landfill-impacted Groundwater Quality Data Set
Parameters which are frequently undetected
Concentrations expressed in mg/L

Statistic	Ammonia	Arsenic	COD	Phenols
Count	870	524	860	794
# Non-detects	52	137	121	467
% Non-Detects	6	26	14	59
Minimum	Values undefined due to uncertainties caused by non-detects			
10th Percentile	0.16			
25th Percentile	1.1			
Median	5.2	0.01	30.6	
75th Percentile	15	0.027	70	0.01
90th Percentile	43.5	0.05	112	0.035
Maximum	200	15.5	2798	8.8
Level of Concern	2	0.01	None	0.001
% Exceeding Level of Concern	57	47	NA	38
Comparative Statistics – Ambient vs. Impacted Data Sets				
Impacted 50th/Ambient 90th Percentile	5.5	0.77	0.81	NA
Ratios Ranked	10	3	5	NA
% Impacted Values > Ambient 90th P	81	43	41	19
% Impacted > Ambient 90th P Ranked	10	4	3	1



Figures 4a- 4d. Frequency percentage histograms showing differences between ambient and impacted data sets for four parameters which are frequently undetected. Non-detects are grouped together in a single bin to the left of the detected values.

3.6 Landfill-impacted groundwater quality in relation to standards and guidance values

Whereas ambient groundwater quality may often exceed applicable standards and guidance values, particularly in the case of iron and manganese, concentrations exceeding standards and guidance values are, as would be expected, much more prevalent in the landfill-impacted data set. When percentages exceeding standards are compared between the two data sets, landfill-impacted groundwater shows higher percentages for all parameters. Increases in percentage exceeding standards rank in the following order: ammonia > TDS > chloride > arsenic > manganese > phenols > iron, again confirming the reliability of ammonia as an indicator of landfill-related water quality impact and the lack of reliability of iron.

4. CONCLUSIONS

This study shows that groundwater quality data generated through sampling of monitoring wells at regulated landfills can provide a valuable resource for characterizing groundwater quality on a regional basis. Within the study area, it is apparent that contemporary data derived from groundwater monitoring wells is different than historical data derived from water supply wells which was previously used to characterize ambient groundwater quality. The biggest differences are seen in the case of iron and manganese and these differences are attributed to differences in sample preparation and turbidity. The contemporary data, which is derived from unfiltered samples, shows higher metals concentrations than the historic data derived from filtered samples and the contemporary data are considered to be more representative of true ambient groundwater quality.

Iron and manganese were the two parameters most commonly detected above the applicable level of concern in ambient groundwater samples. Iron exceeded its New York State groundwater quality standard (0.3 mg/L) in 75 % of the samples and manganese exceeded its USEPA drinking water guidance value (0.05 mg/L) in 65 % of the samples. Unlike iron, which is considered to be an aesthetic rather than a health concern, the widespread occurrence of manganese at concentrations above its health based guidance value may be of significance from the public health standpoint. Arsenic, which exceeds the federal MCL from drinking water in 11 percent of the samples, is also of potential health significance due to its well-documented human health effects.

Of the ten parameters studied ammonia, manganese and alkalinity were found to be the most reliable indicators of landfill-derived groundwater quality impact and iron and total phenols were found to be the least reliable.

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