

## Radionuclides and Inorganics in Selected Drinking Water Sources

### Introduction

The water wells in the immediate vicinity of the WIPP site provide water primarily for livestock, industrial usage by oil and gas production operations, and monitoring studies conducted by various groups. In March 2000, water samples were collected for CEMRC environmental monitoring studies from six sources in the region of the WIPP. The sources included the community water supplies of Carlsbad, Loving, Otis, and Hobbs; the water supply for the WIPP site (Double Eagle); and one private well.

Aquifers in the region surrounding the WIPP include Dewey Lake, Culebra-Magenta, Ogalalla, Dockum, Pecos River alluvium and Capitan Reef. The main Carlsbad water supply is the Sheep Draw well field whose primary source is the Capitan Reef aquifer. The Hobbs and WIPP-Double Eagle water supplies are drawn from the Ogalalla aquifer, while the Loving/Malaga and Otis supply wells draw from deposits that are hydraulically linked to the flow of the Pecos River. The source for the sampling site designated as Private Well #2 is a well seven miles southwest of the WIPP; this water is drawn from the Culebra aquifer.

The 2000 drinking water samples were collected after WIPP began receiving radioactive waste (March 1999), but before the WIPP began receiving mixed waste (September 2000). Therefore, this summary represents monitoring phase data for radionuclides in drinking water but continues the baseline phase for non-radiological constituents.

CEMRC began collecting drinking water samples in 1997, and summaries of methods, data and results from previous sampling were reported in the CEMRC 1997, 1998 and 1999 reports (available at <http://www.cemrc.org>). The results of previous analyses of drinking water were generally consistent for each source across sampling periods, with few organic contaminants detected and inorganic substances mostly below levels specified under the Safe Drinking Water Act.

### Methods

All 2000 samples were collected according to EPA protocols for the collection, handling and preservation of drinking water as follows: (1) 4 L for radiological analyses, (2) 1 L for elemental analyses and (3) 1 L for anion tests. None of the samples were filtered before analysis, but a portion of the 4-L sample was transferred to a 3-L Marinelli beaker for gamma spectroscopy analyses. The 2000 samples were collected at the same six locations as the 1999 samples.

CEMRC performed non-radiological analyses of drinking water samples using IC, ICP-MS and AAS. Instrumentation, general methods and QA/QC results are presented in Appendix K. CEMRC did not test the 2000 drinking water samples for organic constituents because of low concentrations and consistent results in prior analyses performed by an external laboratory.

Radiological analyses were carried out at CEMRC by first counting the samples in Marinelli beakers using a coaxial, high purity Ge detector system to determine gamma-emitting radionuclide activity concentrations. Radiochemistry was then applied to each sample for actinide separation and purification using multiple precipitation, co-precipitation and ion-exchange and/or extraction chromatography. Once the actinides were separated elementally, they were co-precipitated with LaF<sub>3</sub> and deposited onto filters, which were then counted on an alpha spectroscopy system. Radioanalytical QA/QC data are presented in Appendix L.

### Results and Discussion

#### *Radiological*

No radionuclides were measured above MDC in 2000 samples as measured by gamma spectroscopy targeting 11 naturally occurring and 12 anthropogenic gamma-emitters. Four naturally occurring actinides (<sup>234</sup>U, <sup>235</sup>U, <sup>238</sup>U, and <sup>228</sup>Th) were detected via alpha spectroscopy in all of the samples from each

location. However, measured levels of  $^{228}\text{Th}$  are considered largely an artifact of the use of  $^{232}\text{U}$  as a tracer during the radioanalytical process. ( $^{232}\text{U}$  decays to  $^{228}\text{Th}$ , resulting in a positive bias in  $^{228}\text{Th}$  measurements).

The uranium isotope activity concentrations in 2000 water samples were quite similar to the 1999 and 1998 samples, with the greatest variations appearing in  $^{235}\text{U}$  measurements. Measured values for samples collected during 2000 were 28-510  $\text{mBq L}^{-1}$  for  $^{234}\text{U}$ , 0.81-12  $\text{mBq L}^{-1}$  for  $^{235}\text{U}$ , and 11-200  $\text{mBq L}^{-1}$  for  $^{238}\text{U}$ . Across all years, the highest levels of all three uranium isotopes were measured in samples from Private Well #2, and lowest levels were measured in samples from Carlsbad (Table 16). Across all years,  $^{234}\text{U}$  concentrations were 3.2-3.4 times greater than  $^{238}\text{U}$  in samples from Loving, and 2.4-2.8 times greater in samples from the other five drinking water sources. Enrichment of  $^{234}\text{U}$  at these levels is common in drinking water produced from underground sources (Eisenbud, M. and T. Gesell, 1997, *Environmental Radioactivity*, Academic Press, San Diego).

For  $^{235}\text{U}$ , the levels measured in 2000 were higher than in both 1998 and 1999 (3-27%) for samples from Carlsbad, Double Eagle and Otis, and higher than the 1998 sample from Hobbs. Similar or lower levels of  $^{235}\text{U}$  were measured in 2000 samples from Loving and Private Well #2 as compared to samples from 1998. For  $^{234}\text{U}$ , the 2000 samples from Hobbs, Loving and Otis were higher than levels measured in 1998. For Carlsbad, Double Eagle, and Private Well #2, the  $^{234}\text{U}$  levels measured in 2000 samples were lower (2-15%) than in 1998 and 1999 samples. For  $^{238}\text{U}$ , the 2000 samples from Double Eagle, Hobbs, Loving and Otis were higher (5-11%) than in 1998, but values for Carlsbad and Private Well #2 were lower (5-21%) than in 1998.

Excluding measurements from Private Well #2, the ranges and ratios of all three uranium isotopes measured in CEMRC samples during 1998-2000 were similar to values from 1992 samples from Carlsbad, Double Eagle and Loving reported by EEG (Kenny, J.W., 1994, *Preoperational Radiation Surveillance of the WIPP Project by EEG during 1992*, EEG-54).

No comparable data for community drinking water sources have been generated in recent years by Westinghouse Waste Isolation Division (WID), the WIPP management and operating contractor. However, analyses have been reported by WID for samples from a single "fresh" water well near the WIPP site. In general, CEMRC values for  $^{238}\text{U}$  and  $^{234}\text{U}$  in samples from Private Well #2 are 60-120% higher, respectively, than those reported for the fresh water well samples collected during 1997-1999 by WID (1998, *Waste Isolation Pilot Plant Annual Site Environmental Report Calendar Year 1997*, DOE/WIPP 98-2225; 1999, *Waste Isolation Pilot Plant Site Environmental Report for 1998*, DOE/WIPP 99-2225; 2000, *Waste Isolation Pilot Plant 1999 Site Environmental Report*, DOE/WIPP 00-2225). With the exception of a measurement of 0.014  $\text{mBq L}^{-1}$  for a 1998 sample,  $^{235}\text{U}$  values reported by WID from this well are 3-4 times lower than for the nearest source tested by CEMRC (Private Well #2).

The levels and ratios measured by CEMRC for these naturally occurring radionuclides are typical of natural variations in ground water (Cothorn, C.R. and W.L. Lappenbusch, 1983, *Health Physics* 45, 89; Luo et al., 2000, *Geochim. Cosmochim.* 64, 867), and agree well with the few directly comparable values reported from studies in the region. Overall the CEMRC measurements are more consistent through time for each source than the cited annual measurements reported by WID. It is important to note that the quantification of  $^{235}\text{U}$  by alpha spectroscopy may be impacted by tailing from the  $^{234}\text{U}$  spectral region. In particular, higher measured levels of  $^{235}\text{U}$  that are accompanied by lower measured levels of  $^{234}\text{U}$  (such as in the Carlsbad and Double Eagle samples) should therefore be interpreted with caution. As previously noted, values for samples collected in 1998 are believed to have been affected by storage of the samples for > 12 months prior to analyses. Despite acidification, such prolonged storage may have allowed U adsorption to the containers, producing a low bias in measured U.

Of the 18 uranium isotope measurements in 2000 samples, 11 were higher than in 1998 samples. Of these, only three values ( $^{238}\text{U}$  for

Double Eagle, Loving and Otis) were above 2 SD (counting error) of the matching 1998 value. The highest of these elevated  $^{238}\text{U}$  values ( $0.052 \text{ mBq L}^{-1}$  for  $^{238}\text{U}$  in the Otis sample) is still less than half of the highest  $^{238}\text{U}$  values reported by WID for the fresh water well near the WIPP site. Based on the comparisons as summarized, other relevant scientific information and results of analyses of other media reported herein, CEMRC concludes that the higher levels of some uranium isotopes in the 2000 drinking water samples from some sources represent a combination of natural variation and analytical artifact, and are not the result of releases from the WIPP.

Pu was not detected in any 2000 drinking water samples. Results of previous tests using thermal ionization mass spectrometry revealed no Pu in samples from the same six drinking water sources (reported in the CEMRC 1999 Report).

### **Non-Radiological Results**

Measurements of inorganic analytes produced by CEMRC from the six drinking water sources showed little variation between years for each source. Differences of  $> 100\%$  between one set of successive years at a single location have been recorded for Ag, Co, Cu, Pb, Th, Zn, nitrate and fluoride. For five inorganic analytes (Fe, La, Mn, Nd and Sb) differences  $> 100\%$  in successive years have been recorded in samples from two or more sources.

With the exception of these instances, the 1998-2000 measurements exhibit a high level of consistency that provides a useful characterization of each source (Table 17). Private Well #2 exhibited the highest levels of Sr, Na, Mg, K, Cu, Co and Ca, and samples from Otis ranked second highest for measured levels of these analytes. Private Well #2 also had the highest levels of Zn and total U (measured by ICP-MS), while measured levels

of Ba were lowest for Private Well #2 and Otis. Total nitrates (not reduced to N) were highest in samples from Otis ( $19\text{-}22 \mu\text{g L}^{-1}$ ) and Loving ( $17\text{-}23 \mu\text{g L}^{-1}$ ). Across all years, samples from Loving were highest in measured Pb levels ( $1.0\text{-}1.4 \mu\text{g L}^{-1}$ ), while Hg was detected only in samples from Hobbs ( $0.009\text{-}0.014 \mu\text{g L}^{-1}$ ). Measured As levels were highest in samples from Hobbs ( $5.6\text{-}6.5 \mu\text{g L}^{-1}$ ) and Double Eagle ( $5.2\text{-}6.6 \mu\text{g L}^{-1}$ ), and these measurements suggest that these drinking water sources would exceed any As standard  $\leq 5 \mu\text{g L}^{-1}$  as has been recently considered for adoption by EPA.

As in previous years, measured levels of chloride and sulfate exceeded reference levels (secondary maximum contaminant levels) in the 2000 samples from Private Well #2 and Otis. Reference levels for Fe and Mn were also exceeded in the 2000 samples from Private Well #2.

These results are not appropriate for use in assessing of regulatory compliance, due to sample collection locations and other methodological details. However, it is noteworthy that the CEMRC results for Carlsbad and Double Eagle drinking water collected during 1998-2000 generally agreed well with measurements published by the City of Carlsbad Municipal Water System (*1999 Annual Consumer Report on the Quality of Tap Water; 1998 Annual Consumer Report on the Quality of Tap Water*) and with measurements published by the Otis Water User Co-Op (*Annual Water Quality Report, 1999*). As noted in the CEMRC 1999 Report, CEMRC values for nitrates are higher than those reported by Carlsbad and Loving, because the city-reported values are actually total N, rather than total nitrates.

Tables presenting drinking water data summarized herein are available on the CEMRC web site at <http://www.cemrc.org>.

**Table 16. Range of Activity Concentrations and Interannual Comparisons for Uranium Isotopes Measured in Drinking Water during 1998 - 2000**

Location	Analyte	Activity Concentration (Bq L <sup>-1</sup> )		<sup>a</sup> RPC (%)	
		<sup>b</sup> Minimum	<sup>c</sup> Maximum	2000:1998	2000:1999
Carlsbad	<sup>234</sup> U	2.8E-02	3.3E-02	-15	-3
	<sup>235</sup> U	7.0E-04	8.1E-04	8	16
	<sup>238</sup> U	1.1E-02	1.4E-02	-21	0
Double Eagle	<sup>234</sup> U	5.4E-02	6.2E-02	-2	-13
	<sup>235</sup> U	1.1E-03	1.4E-03	27	27
	<sup>238</sup> U	2.0E-02	2.3E-02	10	-4
Hobbs	<sup>234</sup> U	8.5E-02	9.1E-02	3	7
	<sup>235</sup> U	2.2E-03	2.5E-03	5	-8
	<sup>238</sup> U	3.8E-02	4.0E-02	5	3
Loving	<sup>234</sup> U	8.2E-02	8.5E-02	2	-1
	<sup>235</sup> U	1.5E-03	1.7E-03	-6	7
	<sup>238</sup> U	2.4E-02	2.6E-02	8	0
Private Well #2	<sup>234</sup> U	5.1E-01	5.3E-01	-2	-4
	<sup>235</sup> U	1.1E-02	1.2E-02	0	9
	<sup>238</sup> U	2.0E-01	2.1E-01	-5	-5
Otis	<sup>234</sup> U	1.3E-01	1.5E-01	8	-7
	<sup>235</sup> U	2.7E-03	3.0E-03	11	3
	<sup>238</sup> U	4.7E-02	5.3E-02	11	-2

<sup>a</sup> RPC = relative percent change; for 2000:1998 = ((2000 concentration - 1998 concentration) / 1998 concentration) \* 100%;  
for 2000:1999 = ((2000 concentration - 1999 concentration) / 1999 concentration) \* 100%

<sup>b</sup> Minimum activity concentration measured in three consecutive annual samples

<sup>c</sup> Maximum activity concentration measured in three consecutive annual samples

**Table 17. Range of Concentrations of Selected Inorganic Analytes in Drinking Water Samples Collected during 1998 - 2000**

Analyte	Unit	Minimum/Maximum Concentrations by Location								
		Carlsbad			Double Eagle			Hobbs		
		<sup>a</sup> N	<sup>b</sup> Min	<sup>c</sup> Max	N	Min	Max	N	Min	Max
Ag	µg L <sup>-1</sup>	1	1.6E-02	1.6E-02	1	2.8E-02	2.8E-02	2	3.5E-03	4.0E-03
Al	mg L <sup>-1</sup>	2	4.4E-03	3.0E-02	2	4.6E-03	7.0E-03	2	5.1E-03	1.0E-02
As	µg L <sup>-1</sup>	3	5.4E-01	5.7E-01	3	5.2E-00	6.6E-00	3	5.6E-00	6.5E-00
Ba	µg L <sup>-1</sup>	3	6.8E+01	7.4E+01	3	6.8E+01	9.0E+01	3	5.7E+01	6.4E+01
Be	µg L <sup>-1</sup>	0	<sup>d</sup> NA	NA	1	3.6E-02	3.6E-02	1	5.4E-02	5.4E-02
Ca	mg L <sup>-1</sup>	3	6.1E+01	7.9E+01	3	4.5E+01	5.5E+01	3	7.0E+01	8.5E+01
Cd	µg L <sup>-1</sup>	1	6.6E-03	6.6E-03	2	2.2E-03	4.0E-03	1	1.4E-02	1.4E-02
Co	µg L <sup>-1</sup>	2	1.5E-01	3.4E-01	3	9.3E-02	1.4E-01	3	1.7E-01	3.6E-01
Cr	µg L <sup>-1</sup>	3	3.0E-01	4.0E-00	3	2.9E-00	3.5E-00	3	2.3E-00	3.1E-00
Cu	µg L <sup>-1</sup>	2	1.8E-00	3.9E-00	3	1.2E-00	3.8E-00	3	1.9E-00	2.1E-00
Fe	mg L <sup>-1</sup>	1	4.3E-03	4.3E-03	2	4.2E-03	9.0E-03	3	4.3E-03	3.6E-02
Hg	µg L <sup>-1</sup>	0	NA	NA	0	NA	NA	3	9.0E-03	1.4E-02
K	mg L <sup>-1</sup>	3	1.3E-00	2.9E-00	3	2.7E-00	3.5E-00	3	2.4E-00	2.9E-00
La	µg L <sup>-1</sup>	2	1.4E-02	4.4E-02	3	1.4E-02	6.3E-02	3	1.3E-02	5.0E-02
Li	µg L <sup>-1</sup>	2	7.3E-00	7.9E-00	3	1.8E+01	1.9E+01	3	2.9E+01	3.2E+01
Mg	mg L <sup>-1</sup>	3	3.0E+01	3.4E+01	3	1.1E+01	1.1E+01	3	2.0E+01	2.1E+01
Mn	µg L <sup>-1</sup>	3	5.5E-02	3.2E-01	3	2.3E-01	3.1E-01	3	2.5E-01	6.7E-01
Mo	µg L <sup>-1</sup>	3	7.0E-01	1.2E-00	3	1.5E-00	2.3E-00	3	2.6E-00	2.7E-00
Na	mg L <sup>-1</sup>	3	2.0E+01	9.9E+01	3	3.1E+01	3.8E+01	3	4.0E+01	4.9E+01
Ni	µg L <sup>-1</sup>	2	1.9E-00	2.1E-00	3	1.1E-00	1.5E-00	3	1.6E-00	2.5E-00
Pb	µg L <sup>-1</sup>	2	3.8E-01	1.5E-00	3	3.2E-01	1.4E-00	3	9.4E-02	1.7E-01
Sb	µg L <sup>-1</sup>	1	2.4E-01	2.4E-01	2	1.9E-02	2.4E-02	2	3.9E-02	4.7E-02
Sn	µg L <sup>-1</sup>	0	NA	NA	1	2.8E-01	2.8E-01	0	NA	NA
Sr	µg L <sup>-1</sup>	3	3.5E+02	4.6E+02	3	5.0E+02	5.3E+02	3	7.9E+02	9.2E+02
Th	µg L <sup>-1</sup>	1	2.5E-02	2.5E-02	2	5.7E-03	3.0E-02	2	4.6E-03	4.6E-03
Tl	µg L <sup>-1</sup>	2	1.2E-01	1.5E-01	0	0.0E+01	0.0E+01	1	4.9E-02	4.9E-02
U	µg L <sup>-1</sup>	2	8.2E-01	8.5E-01	3	1.7E-00	1.8E-00	3	3.0E-00	3.4E-00
V	µg L <sup>-1</sup>	3	3.8E-00	4.7E-00	3	1.8E+01	2.7E+01	3	2.2E+01	3.6E+01
Zn	µg L <sup>-1</sup>	3	4.6E-00	1.5E+01	3	1.5E-00	4.2E-00	3	8.4E-01	3.4E-00
Nitrate	mg L <sup>-1</sup>	3	3.5E-00	5.9E-00	3	1.1E+01	1.4E+01	3	1.7E+01	2.0E+01
Chloride	mg L <sup>-1</sup>	3	1.5E+01	1.9E+02	3	2.6E+01	3.7E+01	3	6.3E+01	9.4E+01
Fluoride	mg L <sup>-1</sup>	3	2.2E-01	7.8E-01	3	5.0E-01	1.0E-00	3	6.2E-01	1.3E-00
Sulfate	mg L <sup>-1</sup>	3	8.1E+01	1.2E+02	3	4.1E+01	5.7E+01	3	1.0E+02	1.4E+02

Table continued on next page

**Table 17. Range of Concentrations of Selected Inorganic Analytes in Drinking Water Samples Collected during 1998 - 2000 (Cont.)**

Analyte	Unit	Minimum/Maximum Concentrations by Location								
		Private Well #2			Otis			Loving		
		<sup>a</sup> N	<sup>b</sup> Min	<sup>c</sup> Max	N	Min	Max	N	Min	Max
Ag	µg L <sup>-1</sup>	3	4.6E-03	3.6E-02	1	2.6E-02	2.6E-02	2	3.3E-03	5.6E-03
Al	mg L <sup>-1</sup>	2	4.6E-03	9.1E-03	1	3.5E-03	3.5E-03	2	3.6E-03	5.0E-03
As	µg L <sup>-1</sup>	3	2.0E-00	2.3E-00	3	1.2E-00	1.5E-00	3	1.2E-00	1.6E+00
Ba	µg L <sup>-1</sup>	3	8.5E-00	9.2E-00	3	1.4E+01	1.8E+01	3	2.9E+01	3.2E+01
Be	µg L <sup>-1</sup>	2	1.1E-01	1.9E-01	0	NA	NA	1	9.4E-02	9.4E-02
Ca	mg L <sup>-1</sup>	3	4.4E+02	5.9E+02	3	2.4E+02	2.5E+02	3	7.8E+01	9.4E+01
Cd	µg L <sup>-1</sup>	3	9.2E-02	1.1E-01	1	6.9E-03	6.9E-03	2	1.0E-02	1.6E-02
Co	µg L <sup>-1</sup>	3	1.0E-00	1.4E-00	2	3.9E-01	5.1E-01	3	1.5E-01	6.4E-01
Cr	µg L <sup>-1</sup>	3	3.1E-00	3.8E-00	3	8.6E-01	4.1E-00	3	2.3E-00	4.3E+00
Cu	µg L <sup>-1</sup>	3	5.2E-00	1.0E+01	2	4.4E-00	5.5E-00	3	2.4E-00	4.7E+00
Fe	mg L <sup>-1</sup>	3	6.6E-01	8.1E-01	2	5.1E-03	1.2E-02	1	2.2E-03	2.2E-03
Hg	µg L <sup>-1</sup>	0	NA	NA	0	NA	NA	0	NA	NA
K	mg L <sup>-1</sup>	3	8.2E-00	8.3E-00	3	3.2E-00	3.9E-00	3	1.9E-00	2.5E+00
La	µg L <sup>-1</sup>	3	1.4E-02	2.2E-02	1	2.9E-03	2.9E-03	3	6.8E-03	2.2E-02
Li	µg L <sup>-1</sup>	3	1.8E+02	2.1E+02	2	4.7E+01	4.9E+01	3	1.7E+01	2.0E+01
Mg	mg L <sup>-1</sup>	3	1.4E+02	1.7E+02	3	8.3E+01	9.1E+01	3	3.5E+01	4.1E+01
Mn	µg L <sup>-1</sup>	3	3.1E+01	8.0E+01	2	1.7E-01	2.5E-01	2	5.2E-02	6.8E-02
Mo	µg L <sup>-1</sup>	3	3.3E+01	3.8E+01	2	2.4E-00	2.7E-00	3	1.4E-00	1.6E+00
Na	mg L <sup>-1</sup>	3	2.1E+02	2.7E+02	3	9.6E+01	1.1E+02	3	1.9E+01	2.3E+01
Ni	µg L <sup>-1</sup>	3	1.4E+01	2.0E+01	2	7.2E-00	7.4E-00	3	2.2E-00	2.7E+00
Pb	µg L <sup>-1</sup>	3	9.5E-02	1.8E-01	2	1.1E-01	2.1E-01	3	1.0E-00	1.7E+00
Sb	µg L <sup>-1</sup>	2	2.2E-02	9.1E-02	2	4.0E-02	4.1E-01	2	6.8E-02	2.5E-01
Sn	µg L <sup>-1</sup>	0	NA	NA	0	NA	NA	0	NA	NA
Sr	µg L <sup>-1</sup>	3	5.6E+03	7.9E+03	3	2.8E+03	2.9E+03	3	6.5E+02	8.3E+02
Th	µg L <sup>-1</sup>	2	4.1E-03	6.0E-03	2	6.6E-03	2.7E-02	2	3.7E-03	1.1E-02
Tl	µg L <sup>-1</sup>	3	2.2E-01	3.6E-01	0	NA	NA	1	5.1E-02	5.1E-02
U	µg L <sup>-1</sup>	3	1.4E+01	1.7E+01	2	4.2E-00	4.2E-00	3	2.0E-00	2.1E+00
V	µg L <sup>-1</sup>	3	1.1E+01	1.9E+01	3	9.4E-00	1.2E+01	3	9.2E-00	1.3E+01
Zn	µg L <sup>-1</sup>	3	2.2E+01	3.9E+01	2	4.4E-00	1.1E+01	3	4.8E-00	7.8E+00
Nitrate	mg L <sup>-1</sup>	3	1.4E-00	3.8E-00	3	1.9E+01	2.2E+01	3	1.7E+01	2.3E+01
Chloride	mg L <sup>-1</sup>	3	4.6E+02	5.0E+02	3	2.7E+02	3.9E+02	3	1.6E+01	2.9E+01
Fluoride	mg L <sup>-1</sup>	3	1.4E-00	2.1E-00	3	5.5E-01	1.3E-00	3	2.5E-01	6.0E-01
Sulfate	mg L <sup>-1</sup>	3	1.9E+03	2.5E+03	3	6.4E+02	7.5E+02	3	1.4E+02	2.0E+02

<sup>a</sup>N = number of samples > MDL<sup>b</sup>Min = minimum measured concentration in three consecutive annual samples<sup>c</sup>Max = maximum measured concentration in three consecutive samples<sup>d</sup>NA = all samples below MDL for analyte