

**The Devil's Details about Radioisotopes and Other Toxic Contaminants in Marcellus Shale Flowback Fluids and Their Appearance in Surface Water Sources and Threats to Recreationalists, Private Well Water Users, and Municipal Water Supplies**

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**March 11, 2011**

In yesterday's FracTracker post, CHEC data manager Matt Kelso told the tale of two stories regarding radionuclides in Marcellus Shale flowback water and in river water as sampled by the PA DEP. As he said "the devil is in the details" and here are the "devils details" that put both stories into the proper public health context.

There are without doubt higher levels of radioisotopes in Marcellus Shale flowback fluids than in the fracking fluids, which are injected under high pressure to fracture the shale layer. And in general problems related to naturally occurring radioisotope buildup in the oil and gas industry are well documented. Following is a passage from my expert testimony in the Matter of Delaware River Basin Commission Consolidated Administrative Adjudicatory Hearing on Natural Gas Exploratory Wells; Filed November 23, 2010-

"Elevated concentrations of naturally occurring radioactive materials (NORM), including  $^{238}\text{U}$ ,  $^{232}\text{Th}$  and their progeny, are found in underground geologic deposits and are often encountered during drilling for oil and gas deposits (Rajaretnam G, and Spitz HB., 2000). Drill cuttings from the Marcellus may be enriched in radium radionuclides and off-gas the radioelement radon. Also, the activity levels and/or availability of naturally occurring

radionuclides can be significantly altered by processes in the oil, gas and mineral mining industries (B. Heaton and J. Lambley, 2000). Scales in drilling and process equipment may become enriched in radionuclides producing technologically enhanced naturally occurring radioactive materials (TENORM). Exposure to TENORM in drilling equipment may exceed OSHA and other regulatory authority standards for the protection of both human and ecological health. The occurrence of TENORM concentrated through anthropogenic processes in soils at oil and gas wells and facilities represents one of the most challenging issues facing the Canadian and US oil and gas industry today (Saint-Fort et al., 2007). The risk of contamination of surface water and ground water by TENORM accompanies the risk of soil contamination, as TENORM generated may runoff of drilling equipment during rain events or if on the soil surface into surface water sources and/or enter groundwater by transport through the unsaturated zone”.

In a review article in Environmental Science and Technology (ES&T), authors Karbo, Wilhelm and Campbell (EPA Region III leads and Office of Radiation and Indoor Air) stated;

“New York’s Department of Environmental Conservation (NYDEC) reported that thirteen samples of wastewater from Marcellus Shale gas extraction contained levels of radium-226 ( $^{226}\text{Ra}$ ) as high as 267 times the safe disposal limit and thousands of times the limit safe for people to drink. The New York Department of Health (NYDOH) analyzed three Marcellus Shale production brine samples and found elevated gross alpha, gross beta, and  $^{226}\text{Ra}$  in the production brine. Devonian-age shales contain naturally occurring radioactive material (NORM), such as uranium (U) and thorium (Th) and their daughter products,  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$ . The Marcellus Shale is considered to have elevated levels of NORMs. NORMs that have been concentrated or exposed to the accessible environment as a result of human activities, such as mineral extraction, are defined by the EPA as technologically enhanced NORM (TENORM).

TENORM may be concentrated because of (1) temperature and pressure changes during oil and gas production, (2)  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  in produced waters reacting with barium sulfate ( $\text{BaSO}_4$ ) to form a scale in well tubulars and surface equipment, (3)  $^{226}\text{Ra}$  and  $^{228}\text{Ra}$  occurring in sludge that accumulates in pits and tanks, and (4) NORM occurring as radon ( $\text{Rn}$ ) gas in the natural gas stream".

If this flowback--produced water with elevated TENORM is disposed of in sewage treatment facilities or other ineffective wastewater disposal processes - then the TENORM level in surface water (the receiving stream or river) will be largely determined by dilution offered by fluid flows within the waste plant and dilution offered by the water flows themselves in the river or stream.

So it is entirely possible that Marcellus Shale flowback and produced fluids (yes I hesitate to call it water because it is contaminated fluid - with many identified toxic contaminants; if this were coming from other industries it would be a hazardous liquid waste) will have elevated levels of TENORM and many other contaminants (see explanation in Appendix 1 below) but levels of TENORM in the surface water it is going into will not exceed background levels, seen in the stream or river system, once it is completely mixed in the stream or river.

But here is the devil in the details as Matt said in his article. Recreationalists' fish and boat around these outfalls (this is documented by CHEC in the Allegheny River Stewardship Project and the Pittsburgh Fish Consumption Project) and we have no idea of the levels of TENORM (or other contaminants) in receiving water near the outfalls before full river mixing occurs.

Additionally we have no idea of the level of long term bioaccumulation of TENORM (and other

contaminants) in fish and other aquatic resources that may frequent or live in areas where this material is disposed of in.

Concentrations of TENORM and the many other contaminants in the effluent from treatment of oil and gas flowback fluids will vary in receiving streams and rivers according to the flow of water in the receiving stream or river and their concentrations in the flowback fluids. Therefore, levels of TENORM in receiving streams and rivers will reach a peak (everything else being equal) during times of low flow- such as a drought or long periods without rain or snowmelt and peak levels will be higher in the surface water near the outfall than downstream in the river after it is mixed completely with water flow from the stream or river. The PA DEP river water samples for radium were not taken during periods of low flow but during the fall season when rain was more plentiful. And they were not taken near outfalls of plants accepting oil and gas waste fluids for treatment, before complete mixing occurs—therefore peak levels in these areas were not captured by their sampling plan.

Additionally, levels of TENORM (and other contaminants) from sewage treatment plants and inefficient brine treatment plants will be higher in low volume streams (such as 10 Mile Creek in Greene and Washington Counties and Blacklick Creek in Indiana County) than in large volume river systems like the Monongahela River. We simply don't know what levels of TENORM are like at peak levels in low volume streams during periods of low flow or in areas just downstream of effluent outfalls before complete mixing takes place.

CHEC has data showing that levels of bromides, barium and strontium exiting the McKeesport POTW (sewage treatment plant-POTW stands for Publically Owned Treatment Plant) vary over a day's sampling; they are dependent on when the slug of produced-flowback brine is introduced into the system and the slug's rate of entry into the treatment system. At the McKeesport POTW, it is customary that the slug of oil and gas waste fluid is introduced into the treatment system at 7 pm. One sees that the levels of these contaminants in outfall effluent raises sharply over a short period of time and then falls back to baseline (See CHEC figures 1, 2 and 3), when the slug is through the system. Any TENORM, in the oil and gas waste fluid being treated, not taken out by the treatment system will reasonably follow the same pattern. That is it will come and go quickly and we have no idea of peak levels of TENORM or any other contaminants in the stream or river near the treatment plant outfall.

What is the solution to all this? Are we to sample continuously; at all treatment plant outfalls, in river and stream segments between treatment plant outfalls and water intakes, at all water intakes and in all finished drinking water (and I might add in private well water systems that may pull in contaminants from nearby streams and rivers) - -across the entire area Marcellus Shale waste fluids are being disposed of (this would include Pennsylvania, New York, Ohio, and West Virginia)? This is exactly what is necessary to be done to assure protection of drinking water supplies, recreationalists, and the health of aquatic resources if we continue to allow oil and gas flowback water to be disposed of in sewage treatment and inefficient brine treatment plants.

NO - this would be cost prohibitive and impractical to do on the scale that is necessary to protect public health and aquatic resources. We must use the precautionary principal here and insist that sewage treatment plants not accept oil and gas wastewater, period. Batches of oil and gas wastewater need to be tested continuously for levels of TENORM and all other possible

contaminants so that a determination can be made of where the fluids can be adequately and safely disposed of. Fluids that are determined to be hazardous and/or toxic should be transported only by certified haulers and loads need to be properly manifested so there is an accurate accounting of the volumes of waste and where it is being sent for ultimate treatment. The technical capabilities and acceptance of brine fluids, of and by, oil and gas waste fluid treatment facilities must be matched exactly to the realities of levels of contaminants in the brine fluids.

The intent of the Resource Conservation and Recovery Act (RCRA) was to insure that there is a "cradle to grave" system to document, handle and dispose of all hazardous and toxic waste from all industries and even municipal authorities in a safe and effective manner. RCRA is basically an extension of the environmental public health precautionary principal; and if implemented and enforced thoughtfully and comprehensively prevents the formation of new Superfund sites and will assure that the public and environmental receptors are protected from contaminants in oil and gas waste fluids- be they called flowback or produced water, or brine or anything else.

Figure 1, Time-plot of Barium concentration in effluent from the McKeesport POTW, sampled beginning 10/19/2010. Hour 1 begins at 19:00 (7:00 PM). A sample was taken on the hour, every hour, for a period of 24 hours.

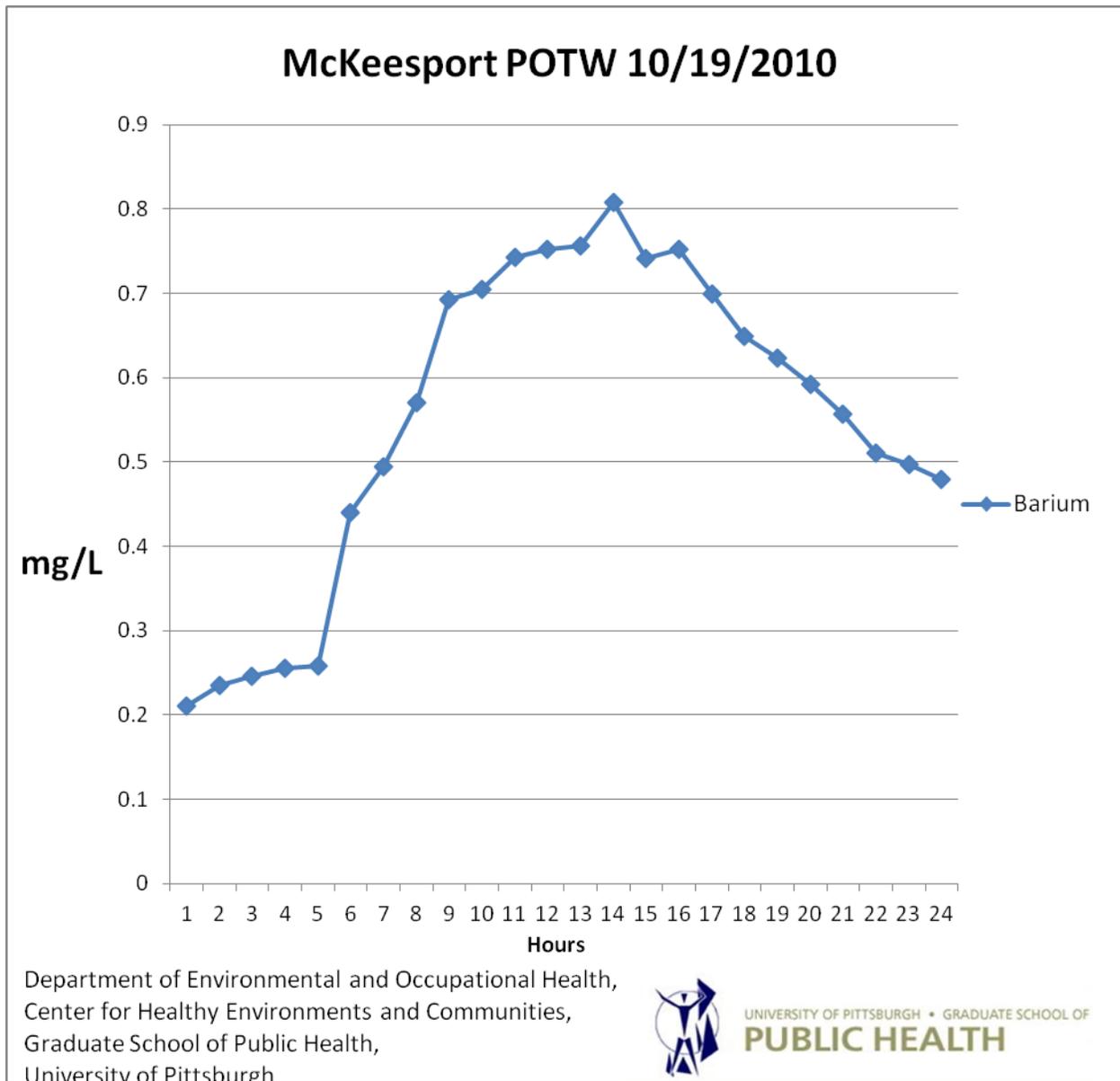


Figure 2, Time-plot of Strontium concentration in effluent from the McKeesport POTW, sampled beginning 10/19/2010. Hour 1 begins at 19:00 (7:00 PM). A sample was taken on the hour, every hour, for a period of 24 hours.

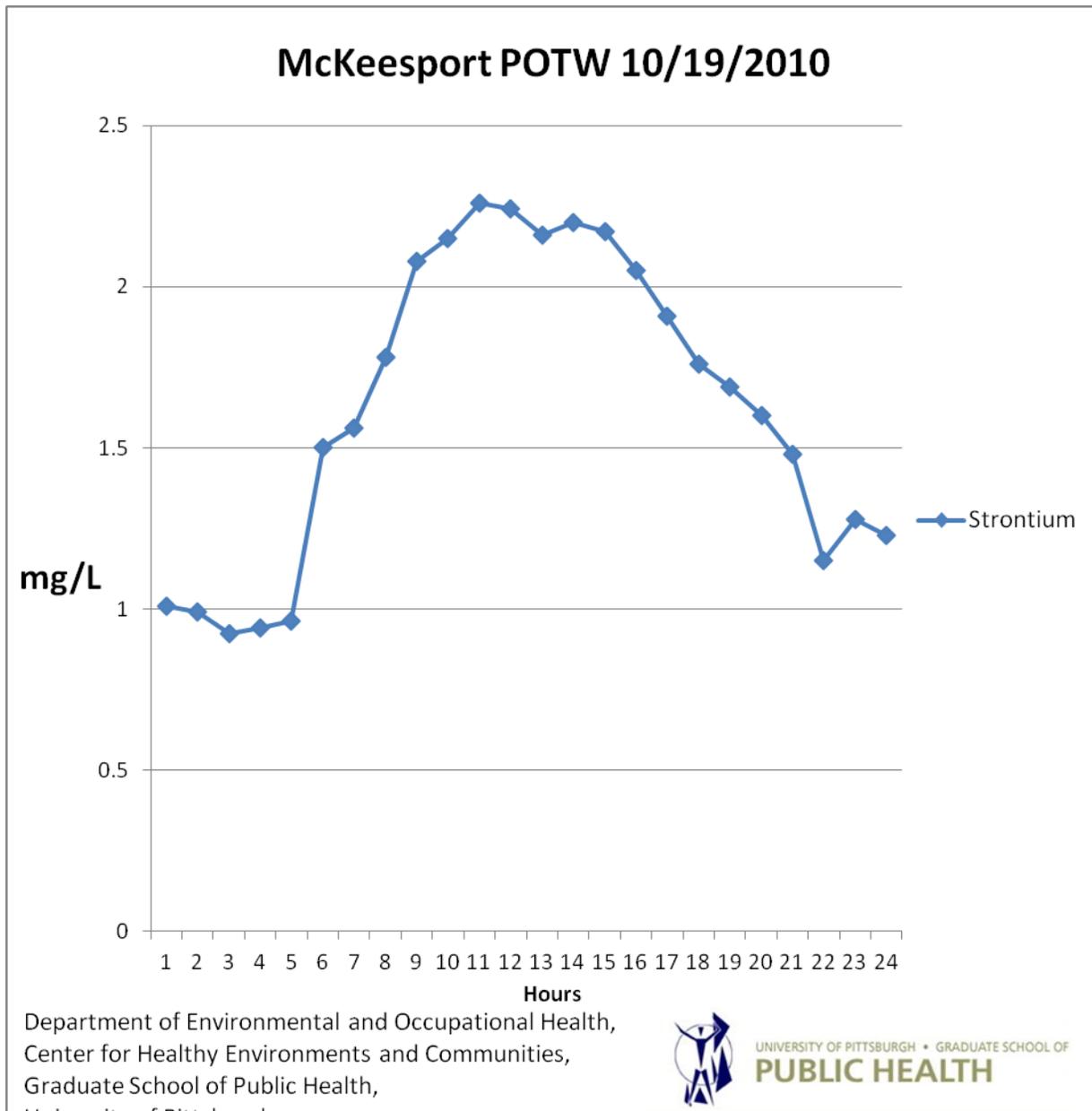
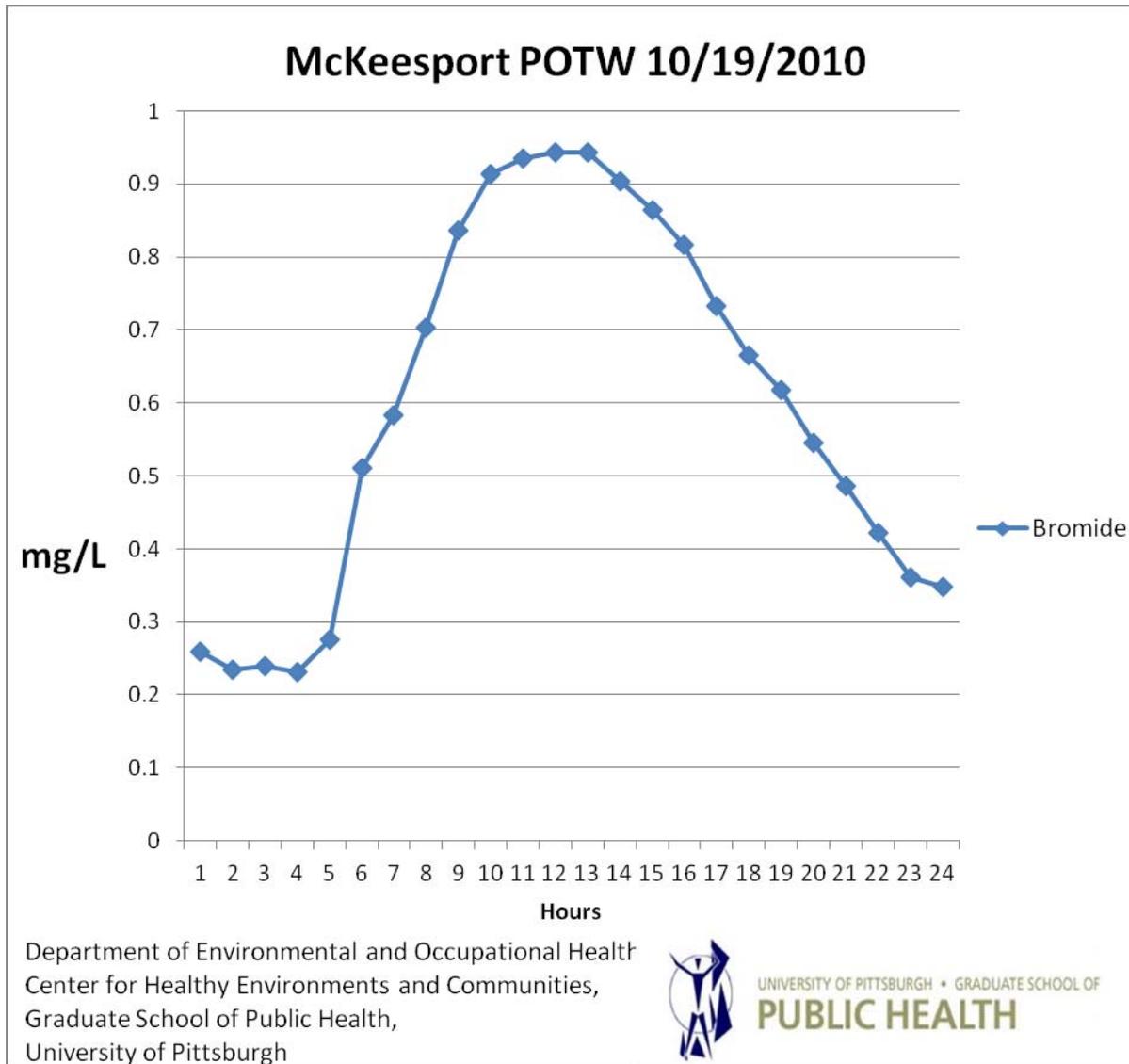


Figure 3, Time-plot of bromides concentration in effluent from the McKeesport POTW, sampled beginning 10/19/2010. Hour 1 begins at 19:00 (7:00 PM). A sample was taken on the hour, every hour, for a period of 24 hours.



Hydraulic fracturing (HF) of shale gas deposits uses considerable masses of chemicals, for a variety of purposes to open and keep open pathways through which natural gas, oil and other production gases and liquids can flow to the well head. HF, also known as slick-water fracturing, introduces large volumes of amended water at high pressure into the gas bearing shale where it is in close contact with formation materials that are enriched in organic compounds, heavy metals and other elements, salts and radionuclides. Typically, about 1 million gallons and from 3-5 million gallons of amended water are needed to fracture a vertical well and horizontal well, respectively (Hayes, T; 2009, Vidic, R.; 2011). Fluids recovered from these wells can represent from 25% to 100% of the injected amended water solution (Vidic R., 2011) and are called “flowback” or “produced” water depending on the time period of their return.

Flowback and produced water contain high levels of total dissolved solids, chloride, heavy metals and elements as well as enriched levels of organic chemicals, bromide and radionuclides – in addition to the frac chemicals used to make the water slick-water. Levels of contaminants in flowback water generally increase with increasing time in contact with formation materials. There is abundant evidence that fluids recovered from this operation have high levels of total dissolved solids, barium and strontium, chlorides and bromides

While there is at present considerable scientific inquiry and even controversy regarding the potential of vertical or horizontal fracturing of shale gas reservoirs to contaminate shallow or confined groundwater aquifers (thus exposing municipal or private well water users to chemicals used in the hydrofracturing process and/or toxic elements, organic compounds, and radionuclides that exist in the formation materials); disposal of oil and gas wastewater/ Marcellus shale brine water in sewage treatment plants or inefficient brine wastewater treatment facilities is a direct exposure threat to public health through ingestion, inhalation and dermal absorption exposure pathways.