

## Fate of MTBE relative to ethanol and benzene in the unsaturated zone

P. HÖHENER, N. DAKHEL, G. PASTERIS, D. WERNER

Swiss Federal Institute of Technology Lausanne (EPFL),  
ENAC-ISTE-LPE, CH-1015 Lausanne,  
patrick.hoehener@epfl.ch

Increasing amounts of oxygenated compounds are incorporated into gasoline to enhance the octane index. Methyl tert-butyl ether (MTBE) has been identified as a major groundwater problem in several US states, which require consequently the replacement of MTBE by ethanol. European policymakers do not consider MTBE, but rather benzene, as a groundwater problem. We performed large-scale outdoor lysimeter experiments studying the fate of fuel compounds in unsaturated alluvial sand underlain by groundwater under relatively dry summer and wet winter conditions.

In a first study (Pasteris et al., 2002), an artificial fuel mixture containing MTBE (5%), 12 typical other petroleum hydrocarbons and tracers was placed at a defined depth in the unsaturated zone. The migration of vapors and of recharge water to the groundwater was studied in summer over a period of 3 months at 14-20°C. Water tracers showed that no recharge water reached the groundwater. MTBE was found to migrate as vapor to the groundwater, disappeared completely from the unsaturated zone within 31 days, but persisted in the groundwater at  $> 1000 \mu\text{g L}^{-1}$  for more than 70 days. A rapid onset of  $\text{CO}_2$  production and  $\text{O}_2$  consumption was observed in the unsaturated zone from the first day of the experiment. First-order aerobic biodegradation rates for individual compounds were obtained from evaluating the vapor profiles in the unsaturated zone. The rates ranged from  $<0.01 \text{ d}^{-1}$  for MTBE up to  $8.7 \text{ d}^{-1}$  for *n*-octane.

To compare the fate of ethanol and benzene relative to MTBE, a second experiment was performed with the fuel mixture plus ethanol (5%), and benzene (1%). The experiment included a cold (0-10°C) period of 41 days without any recharge, followed by a warmer (5-12°C) period of 30 days with 5 mm recharge per day.  $\text{CO}_2$  production rates were significantly smaller than during the summer experiment and followed temperature changes. MTBE and benzene, but not ethanol, migrated to the groundwater. The center of the ethanol mass remained in a stable position at the place of original burial in the unsaturated zone.

The experiments illustrate the recalcitrance and mobility of MTBE vapors relative to other fuel compounds and ethanol. They allow furthermore to validate reactive transport models for groundwater risk assessment at fuel-contaminated sites.

### References

Pasteris, G., Werner, D., Kaufmann, K., Höhener, P., 2002. Vapor phase transport and biodegradation of volatile fuel compounds in the unsaturated zone: a large scale lysimeter experiment. *Environ. Sci. Technol.*, 36, 30-39.

## Xenon Isotopes in Nanodiamonds

G.HOLLAND<sup>1</sup>, J.D. GILMOUR<sup>1</sup>, A.B. VERCHOVSKY<sup>2</sup> AND G.TURNER<sup>1</sup>

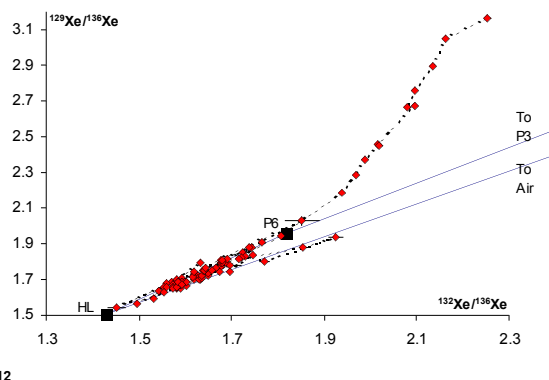
<sup>1</sup>Department of Earth Sciences, University of Manchester,  
Oxford Road, Manchester, M13 9PL. U.K. Email:  
gholland@fs1.ge.man.ac.uk

<sup>2</sup>PSSRI, Open University, Milton Keynes MK7 6BT. Email:  
A.Verchovsky@open.ac.uk

**Introduction:** Nanodiamonds isolated from primitive meteorites contain isotopically 'normal' Xe-P3 and exotic components. Here we discuss the excesses of  $^{129}\text{Xe}$  from  $^{129}\text{I}$  decay that are also observed [1] in the light of data obtained from size-separated Efremovka nanodiamond samples produced at the Vernadsky Institute, Moscow [2].

**Results:** We have previously shown [3] that excess  $^{129}\text{Xe}$  is present in low temperature releases from the large-grain size separate (ED9: 1.5 - 9nm but not in the remainder (ED2,3,4:  $<3 \text{ nm}$ ). Recent analyses of ED12 - a still coarser separate - confirm this tendencies.

**Discussion:**  $^{129}\text{Xe}$  excesses are widespread in nanodiamond separates [1]. Step-heating release patterns suggest that excess  $^{129}\text{Xe}$  shares a site with Xe-P3, but ratios of excess  $^{129}\text{Xe}$  to Xe-P3 vary with extent of parent body processing of the host meteorite. Nanodiamonds from meteorites less processed than reduced CV3 meteorites have similar  $^{129}\text{Xe}$  concentrations but decreasing concentrations of Xe-P3. Greater degrees of processing have led to  $^{129}\text{Xe}$  loss. These observations are most readily explained if the nanodiamond  $^{129}\text{Xe}$  excess was present as  $^{129}\text{I}$  during processing, xenon loss from this site being associated with a parent body process, as for other components [4]. The data constrain the trapping of the P3 component within 10 Ma before parent body processing, unless even the most P3-rich nanodiamonds have lost  $>85\%$  of their original Xe-P3. Xe-HL, Xe-P6 and implications for nucleosynthesis are discussed in an accompanying abstract[5].



### References:

[1] Huss G. R. and Lewis R. S. (1994a) *Meteoritics* **29**, 791-810. [2] Verchovsky A. B. et al. (1998) *Science*, **281**, 1165-1168. [3] Gilmour J. D. et al. (2002) MAPS (abstract in press) [4] Huss G. R. and Lewis R. S. (1994b) *Meteoritics* **29**, 811-829. [5] Turner G. and Gilmour J. D. (2002) *This volume*.