

# Rebound or Recontamination

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In situ thermal remediation (ISTR) is a robust suite of technologies used to treat volatile and semi-volatile organic compound (VOC and SVOC) source zones (Davis, 1997). Often, guarantees are provided for the remedy with the requirement to meet certain numerical goals. Upon observing indicators that the remedy has achieved the goals, such as reaching target temperatures or asymptotic vapor concentrations, the authors recommend collecting confirmatory soil or groundwater samples, which could include several rounds to ensure concentrations remain below the targets.

At some sites, we may see an increase in groundwater concentrations in the months following remediation. This paper discusses potential mechanisms for increased concentrations post ISTR and how to determine why it occurred.

## Defining Rebound and Recontamination

Rebound is an increase in the dissolved phase concentration caused by contaminants residing in the solid phase (as a separate phase or adsorbed) dissolving back into the water, after the water concentrations were reduced by the remedy. It is often caused by diffusion of contaminants of concern (COCs) out of low-permeability layers into the more permeable zones where the remedy was more effective. Therefore, rebound is caused by the partial effectiveness of the remedy, which is more effective for the dissolved components in permeable units than for the COCs residing in the low permeability strata.

Recontamination looks similar to rebound in that it is an increase in dissolved phase concentrations in monitoring wells after the remedy. It is different, though, because recontamination occurs by contaminants outside, below or above the treatment volume migrating into the treated zone. While most apparent in groundwater samples, this recontamination may also cause soil concentrations to increase, as migrating fluids are part of the analysis conducted on soil samples.

There is a clear distinction between rebound and recontamination:

- Rebound results when incomplete remediation of the target volume occurs. It may be caused by insufficient energy input, poor vapor extraction efficiency, or that the remedy is stopped too soon.
- Recontamination results when significant outside contamination migrates into the treatment volume.

It is important to distinguish between rebound and recontamination. Rebound indicates that more treatment is needed for the same volume, whereas recontamination means that treatment is required outside of the original target volume.

## Temperature targets and removal mechanisms

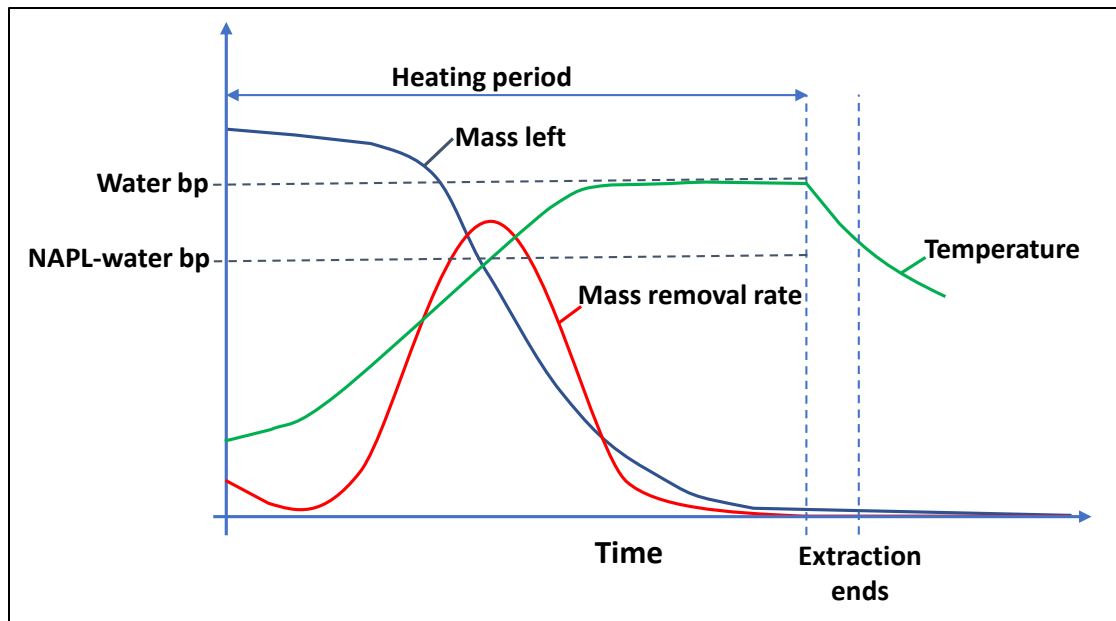
For VOCs, most thermal projects will have a target temperature close to the boiling point of water. At this temperature, the groundwater or soil moisture will boil, and many hundred pore volumes of steam are generated and extracted.

For dense non-aqueous phase liquid (DNAPL) sites, the DNAPL zones will boil at a lower temperature due to the eutectic or co-boiling effect of two liquids. When the sum of the vapor pressures reaches

ambient pressure, boiling begins. For PCE this co-boiling temperature is 87°C; for TCE, 73°C. Once the subsurface reaches the eutectic temperature, DNAPL and water boil until there is no more DNAPL present. The steam acts as a carrier gas and contaminant mass is removed in the vapor phase from the vadose zone. Typically, the peak mass removal rate occurs when the DNAPL zones pass through the co-boiling point range. Once the DNAPL is removed, the boiling point increases to that of water, or 100°C.

For practical reasons, typical temperature targets will allow for flexibility in the target temperature. In the vadose zone the applied vacuum usually lowers the boiling point. Further, temperature sensor accuracy varies. It is typical to allow for some localized outliers or to apply a statistical approach where 90 or 95% of the sensors must meet the targets along with an average temperature goal.

Figure 1 illustrates the site temperature and mass removal during and after heating.



**Figure 1. Mass removal rate, mass left in the target volume, and temperature of the thermal treatment zone as it develops for a typical project. Note that the peak mass removal occurs before the temperature stabilizes near the boiling point of water. Extraction stops a few weeks after the heating phase.**

Near the end of thermal treatment, multiple lines of evidence are used to determine when it is prudent to stop heating:

- Sufficient energy has been delivered to reach target temperatures and boiling conditions.
- The mass removal rate has peaked and since decreased to low levels.
- Interim samples of soil and water indicate COC concentrations below target values.

After the heating period, extraction will continue until all the steam in the formation has been removed or condensed. This allows the site groundwater level to stabilize and fluids to move minimally in the subsurface. This occurs when the pressure reaches atmospheric pressure, which typically takes less than a week. During this time, the site cools by 1 to 5 degrees Celsius, depending on size, shape and groundwater flow rates.

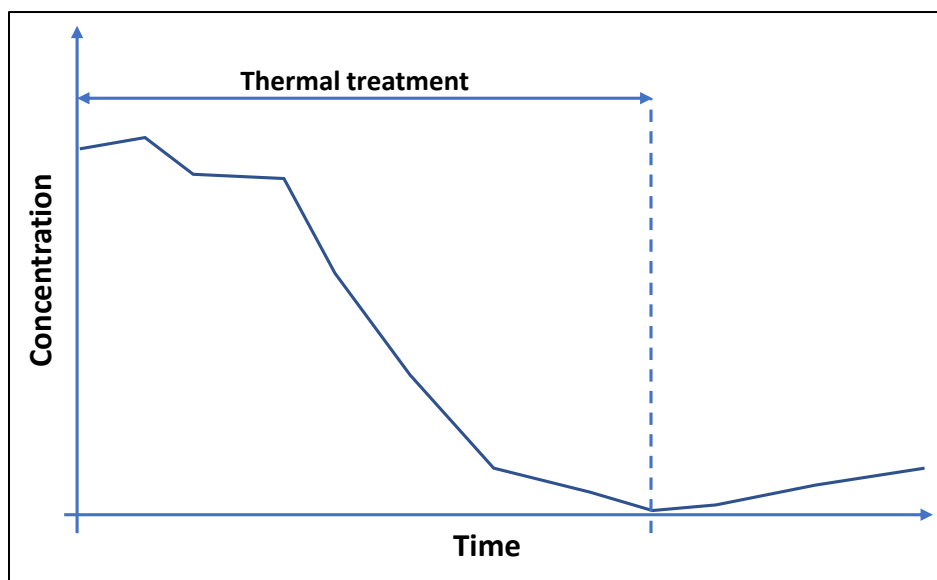
Extraction of fluids is terminated when the site has cooled for a few weeks and no more steam is present, pressures are ambient and temperatures are a few degrees below the target temperature for the

remediation. At this point any rebound or recontamination from adjacent zones caused by the steam condensation will have occurred.

### Rebound – An Example

Rebound is more often observed when using fluid-based remedial technologies. It occurs when COCs diffuse back into the water following remediation. Rebound is caused by contaminant mass residing in the solid phase. Rebound is not commonly observed following thermal remediations, as mass is treated in the solid phase. For ISTR, while usually not observed, rebound could result from incomplete removal of COCs that may partition into the groundwater as it cools and moves after heating.

Figure 2 shows a theoretical example of rebound occurring after thermal treatment. Concentrations start to increase slowly after the system is turned off. This would occur inside of the source zone and not necessarily near the perimeter, where concentrations are lower.



**Figure 2. Rebound in dissolved concentrations caused by incomplete source treatment. Note the slow increase caused by dissolution and/or back-diffusion from partially treated layers. Conceptual sketch – not data from a site.**

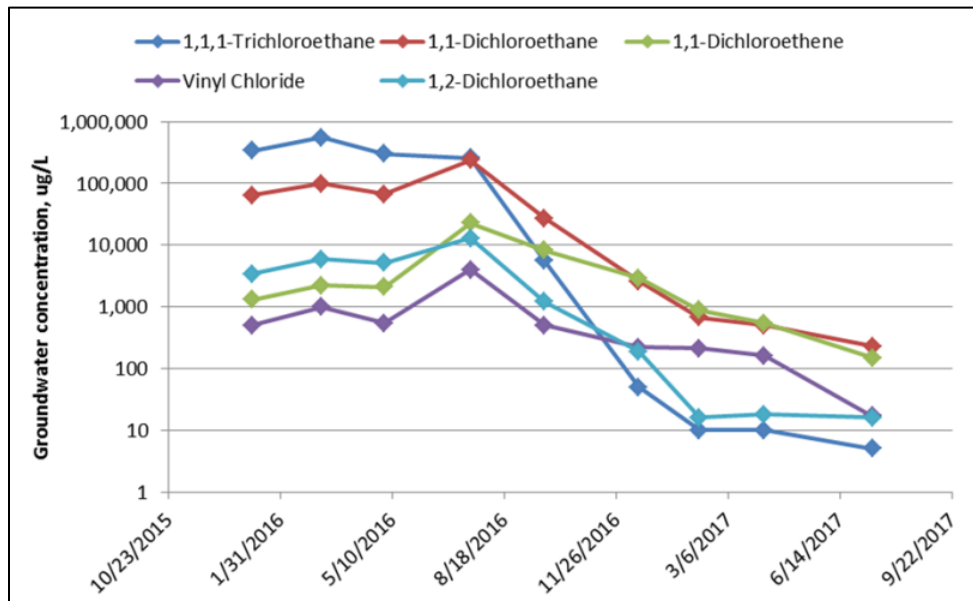
Soil sampling is the best approach to verify conditions that will not result in rebound, as the phase that would contain the COCs is sampled. If soil concentrations are reduced satisfactorily, rebound will not occur.

### Recontamination – Examples

Contaminants outside of the target treatment zone (TTZ) may migrate inwards during and after ISTR operations. It is normal and good practice to extract enough liquids and vapors to create inward gradients for subsequent capture. When this leads to inward migration of COCs, the contaminant mixture is typically similar to the untreated mixture. As the outside area has not been subjected to steam distillation, inwardly migrating contaminant mixtures are composed of both lighter and heavier COCs.

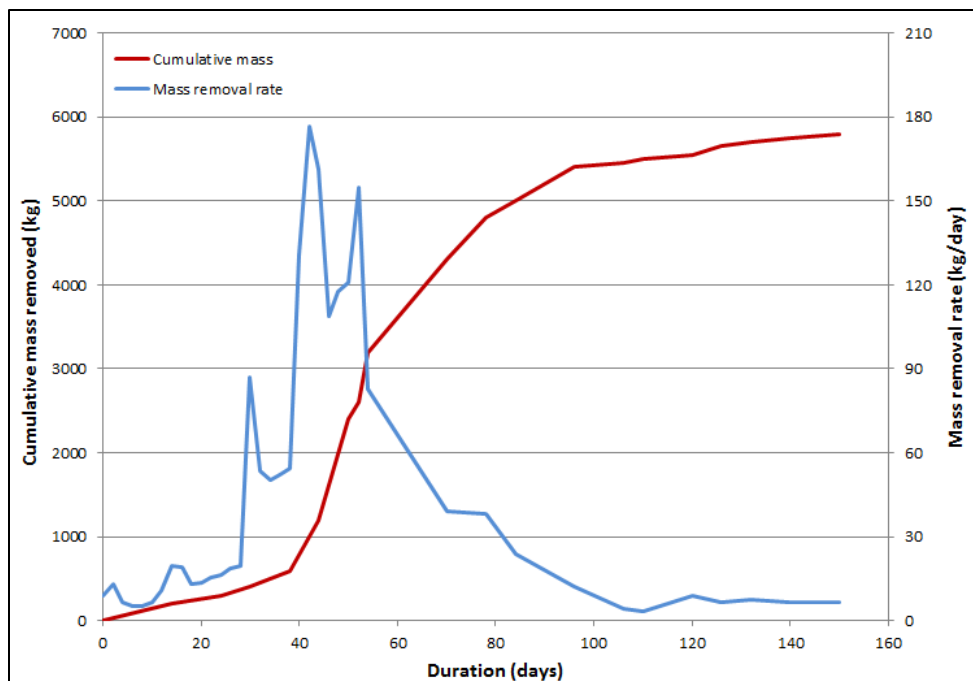
Signs of outside COCs include groundwater monitoring wells near the perimeter, top, or bottom of the TTZ, with dissolved COC levels that plateau at levels above cleanup goals. Another sign can be significant mass removal after the target volume has been thoroughly treated, indicating that mass is flowing in.

Figure 3 shows an example of outside mass causing elevated dissolved concentrations near the perimeter. Near the end of the operational period, even vinyl chloride is observed in the water. As vinyl chloride is extremely volatile, it is not found inside of a well heated TTZ. This data indicates that the COCs are entering from untreated regions below or outside the target volume.



**Figure 3. Dissolved groundwater concentrations in a monitoring well near the TTZ perimeter suspected of outside-in migration of plume water. Note the near-constant ratio of the different COCs in the water near the end of the heating period.**

Figure 4 shows the mass removal curve from a confidential site where mass was found outside of the original treatment zone. A near steady supply of about 5 kg/day of contaminant was found to be flowing in with the extracted water and vapors. This inflow caused the mass removal to remain steady, even after the goals were met in the original target volume, as confirmed via soil sampling. Additional drilling and sampling confirmed DNAPL in the adjacent soils and bedrock.



**Figure 4. Mass removal rate and cumulative mass from a thermal conduction heating (TCH) site, showing mass entering from the outside and no clear drop in removal rate during days 110-150 (Heron et al. 2008).**

The best way to prevent recontamination is to perform complete delineation of the TTZ. When it occurs, the treatment volumes should be expanded to include the zone from where the mass is flowing in.

### **Can condensation of vapors when the heating is turned off create rebound?**

It is well-known that when the system functions as desired, ISTR transfers volatile COCs to the vapor phase, with subsurface air and generated steam migrating to extraction wells. Near the end of treatment, most of the treatment volume will be near boiling temperatures. When heating stops, the site begins to cool and the steam and vapors may condense.

To answer the question of whether this increases groundwater concentrations, a closer look at the phase distribution and mass removal is required. A key factor in thermal treatment is the generation of steam and extraction of this steam during the three to six months of treatment. Near the end of thermal treatment, typically more than 500 pore volumes of steam have been generated and removed via vapor extraction (Heron et al. 2013). The mass removal peak will have passed, and the system will be near diminishing returns. Concentrations in the extracted vapors will have declined to low parts per million volume (ppmv) or parts per billion volume (ppbv) levels. This means that the mass of COC in the last pore volume of steam is miniscule compared to the starting mass. Even if all the steam condensed without being extracted, soil and groundwater concentrations could not increase significantly. The COC mass in that steam would be from the last few days of heating when concentrations are very low.

To minimize the risk of COC condensation, vapor extraction typically continues a minimum of a week after the heating is stopped. This extraction leads to five to 10 additional pore volume exchanges and flushing of the treatment volume.

It should be noted that outside contamination is another matter. When the steam condenses at the end of treatment, groundwater and vapor will flow in to replace the volume, which condenses. This can be slowed or prevented by injection of clean water into the heated zone, another rare but possible alternative.

### **Back diffusion from clay layer – is it rebound?**

If wells screened above a clay aquitard increase in concentration after the remedy, it may be caused by back diffusion, essentially COC mass moving up into the aquifer via diffusion (Chapman and Parker, 2005). It is important to distinguish whether this is rebound or recontamination:

- If the clay aquitard was included in the target treatment volume, it is rebound because the remedy was insufficient.
- If the clay layer is below and therefore outside the target volume, it is recontamination.

Including the top of an aquitard layer in the treatment volume is good practice if significant COC mass is present in this depth interval. Many DNAPL sites contain DNAPL above an aquitard with substantial mass diffusing in.

### **Make sure the source is properly delineated**

Knowing where the contaminant mass is prior to ISTR is essential. This will minimize the risk of recontamination. During the installation of the ISTR subsurface components, the data density of the treatment volume increases dramatically, thereby improving the conceptual site model (CSM). If perimeter sampling indicates high concentrations of contaminants, TRS Group recommends advancing additional borings, thus expanding the perimeter, until encountering low concentrations.

### **The Authors**

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### **References**

Chapman, S.W. and B.L. Parker. 2005. Plume persistence due to aquitard back-diffusion following dense nonaqueous phase liquid source removal or isolation. *Water Resources Research*, Vol. 41, W12411.

Davis, E. L. 1997. How Heat Can Accelerate In-situ Soil and Aquifer Remediation: Important Chemical Properties and Guidance on Choosing the Appropriate Technique. US EPA Issue paper, EPA/540/S-97/502.

Heron, G., R.S. Baker, J.M. Bierschenk and J. LaChance. 2008. Use of Thermal Conduction Heating for the Remediation of DNAPL in Fractured Bedrock. Paper P-003, in: Bruce M. Sass (Conference Chair), *Remediation of Chlorinated and Recalcitrant Compounds—2008. Proceedings of the Sixth International Conference on Remediation of Chlorinated and Recalcitrant Compounds* (Monterey, CA; May 2008). Battelle Press, Columbus, OH.

Heron, G., J. LaChance, and R. Baker. 2013. Removal of PCE DNAPL from Tight Clays using In Situ Thermal Desorption. *Ground Water Monitoring and Remediation*, 33(4): 31-43.