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Emulsified Vegetable Oil Transport Studies in Soil Columns

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ABSTRACT: Column studies were conducted to evaluate the distribution of various forms of emulsified vegetable oil (EVO) with different injection strategies and to evaluate alternative methods for detecting vegetable oil. The demonstrations used Terra System's Slow Release Substrate (SRS®) with an average droplet size of 0.4 microns (µm) and SRS-Fractured Rock (SRS-FR) with an average droplet size of 2.5 µm. Both products each contained 4.0% sodium lactate solution, 60% vegetable oil, food grade emulsifying agents, and nutrients. The studies were conducted using medium to fine grained sandy soil taken from Dover Air Force Base (DAFB), DE. Two different application methods were evaluated for each EVO: 1) dilution of 1 part EVO with 4 parts water (12% oil) followed by chase water and 2) dilution of 1 part EVO and 61.5 parts water (0.96% oil). The appearance of oil droplets, specific conductivity of a sodium chloride tracer, total organic carbon (TOC), volatile fatty acids or VFA (acetic, butyric, lactic, proprionic, and pyruvic acids), and fatty acid methyl esters (FAME: palmitic, stearic, oleic, linoleic, arachidic, and linolenic acids), and hexane extraction of the oil from soil were used as measures of the EVO transport. Injection of a 1 part EVO with 4 parts water mixture followed by chase water allowed for greater transport of the emulsion than injection of the more highly diluted EVO mixture. The smaller droplet size formulation moved through the soil column easier, providing better distribution throughout the formation. The EVO was only detected in the effluents from the soil columns after about one pore volume. FAME analysis of water samples proved useful in determining the presence of vegetable oil in the sample whereas TOC also measures lactate. Hexane-extraction and FAME analysis for soil are both useful methods in determining the presence of vegetable oil in soil samples.

INTRODUCTION

Emulsified vegetable oils (EVO) have been widely applied to promote the anaerobic dechlorination of chlorinated solvent contaminants in groundwater (ESTCP, 2006). The EVO can be applied to treat an entire source area or as a series of permeable reactive biobarriers for plume treatment. The EVO can either be diluted partially followed by chase water or fully diluted to the desired volume. The transport of EVO in a particular soil is affected by the oil retention of the soil, the volumes of EVO and dilution/chase water applied, and the application method (i.e., injection by direct push equipment such as a Geoprobe or gravity feed or pumped into injection wells). These studies investigated whether there would be greater transport of the EVO with the partial dilution of the EVO followed by chase water or with a full dilution of the EVO without additional chase water.

The column studies used a moderate droplet size EVO averaging 2.5 µm and a smaller droplet size EVO with an average of 0.4 µm. Two different application methods were evalu-

ated for each type of EVO: 1) dilution of 1 part EVO to 4 parts water (12% oil) followed by chase water and 2) dilution of 1 part EVO to 61.5 parts water (0.96% oil).

METHODS

Column studies were conducted to evaluate the distribution of EVO using different injection strategies and to evaluate alternative analytical methods for detecting the vegetable oil. The demonstration used Terra System's Slow Release Substrate (SRS®) and Fractured Rock (SRS-FR) products, both containing a 4% sodium lactate solution and 60% vegetable oil. The SRS has a mean droplet size of 0.4 µm and the SRS-FR has a mean droplet size of 2.5 µm. Columns (45.7 cm tall by 5.08 cm diameter) were prepared with 925 or 1,200 g of DAFB soils (a fine to medium grained sand) having a porosity of 0.49 to 0.55 as packed. The columns were gravity fed or pumped utilizing a peristaltic pump to simulate injection of EVO at the field scale.

The following methods were used to evaluate the distribution of the EVO in the water and soil sample phases.

Visible and Microscopic Detection. EVO can be detected visually as a slight milky solution at a concentration of approximately 50 parts per million. In addition, samples were examined using a digital microscope for the presence of the oil droplets.

Specific Conductivity. Oakton® Acorn™ Con 6 meter and probe were used to monitor specific conductivity of a sodium chloride tracer added to some of the EVO solutions.

TOC Analysis. Groundwater samples are analyzed for TOC using HACH low-to-high-range TOC test kits with a HACH DR5000 Spectrophotometer measured at 598 and 430 nanometers (Bloom et al. 2008). TOC was determined by acidifying a sample, sparging it to remove the inorganic carbon, placing an aliquot of the sample in a prepared TOC acid digestion vial containing persulfate, and a pH indicator reagent tube. The sample was then heated and the heating process caused a reaction between the persulfate and acid, producing carbon dioxide. The carbon dioxide diffused into the pH indicator reagent tube and formed carbonic acid, which reacted with the indicator reagent and changed the color of the reagent tube to represent the amount of organic carbon present in the sample.

Volatile Acids (VA). VAs are analyzed using a HACH method that converts fatty acids to acetic acid for analysis with a HACH spectrophotometer. The procedure involved esterification of the VA in the sample with ethylene glycol, sulfuric acid, and heat, followed by the addition of hydroxyalamine hydrochloride, sodium hydroxide, and ferric chloride sulfuric acid. Results are then reported as acetic acid equivalents. Some samples were analyzed for VFAs (acetic, butyric, lactic, proprionic, and pyruvic acids) by ion chromatography.

Fatty Acid Methyl Esters (FAME). Soil or groundwater samples are collected in glass sampling containers. Groundwater samples are filtered using membrane filters of a specific micron size depending on the vegetable oil droplet size. The filter was removed and placed in a small sampling vial equipped with a screw-on lid. Methanolic 3N hydrochloric acid was added to the vial to assist in the breakdown of the vegetable oil triglycerides to methyl esters. The vial was capped, placed in a digester, and heated at

70 degrees Celsius for 20 minutes. After digestion, the sample was cooled to room temperature. Hexane and water were added to the vial and the sample was shaken vigorously to allow the methyl esters to partition into the upper hexane layer. An aliquot of the hexane layer was collected via syringe and manually injected on-column into a Gas Chromatography (GC) equipped with a flame ionization detector (FID) for detection of the methyl esters. Soil samples were treated in the same manner, except that vegetable oil was first extracted from the soil with hexane. The upper layer of the extraction solution was then passed through the membrane filter, removing any leftover solid particulates behind. This method is only semi-quantitative.

Hexane Extraction. The hexane-extractable oil was determined by transferring 10 g of the soil to a beaker, adding 5 g anhydrous sodium sulfate, and mixing to dry the soil. Then two 10 mL aliquots of hexane were added to the soil. The hexane was transferred to an aluminum foil weigh boat and the hexane allowed to evaporate in a fume hood. The resulting weight of extracted oil was then recorded.

RESULTS

Column Study 1—Gravity Feed of SRS-FR. The first column studies were performed under gravity feed. Solutions of 10 mL SRS-FR with 40 mL tap water followed by 138 mL chase water and fully diluted SRS-FR (8 mL EVO to 492 mL tap water) were prepared and added to the top of two soil columns each containing 925 g of DAFB soil. Based on other soil columns, one pore volume would be equivalent to about 283 to 318 mL. Table 1 presents the results for the two gravity-feed columns. Four aliquots of 150 mL tap water were first run through each column and the total recovery of fluid was determined and flow rates were calculated. For column 1, the first aliquot of water passed through the column with a recovery of only 32 mL (most of the water was retained in the pore space of the column). The flow rates of the second through fourth aliquots of tap water for column 1 declined from 5.7 to 2.1 mL/min. Column 2 showed similar results with flow rates of only 0.7 mL/min for the first 150 mL aliquot and decreasing flow rates of 3.9 to 1.9 mL/min for the second through fourth aliquots. Emulsion was not detected in the effluent of Column 1 with the first aliquot of SRS-FR diluted 1:4 chased with 138 mL tap water. The SRS-FR emulsion was detected in the effluent after 135 mL of the second aliquot of SRS-FR diluted 1:4 chased with tap water. This is equivalent to about one pore volume. The emulsion was detected in the third aliquot after 50 mL, but was not observed in the fourth aliquot. The flow rates through this column ranged from 2.5 to 3.5 mL/min. With the more dilute SRS-FR solution, the emulsion was not visibly detected in the effluent after three applications of a total of 450 mL (about 1.4 to 1.6 pore volumes). The columns were taken down and each divided into five sections and the amount of oil retained in each section was measured using hexane-extraction method (Table 2). The highest oil content in column 1 with the partially diluted SRS-FR was in the middle section (580 mg/kg) with less oil in the fourth section and no detectable oil in the final section at the bottom of the column. Only about 266 mg of the 22,080 mg of oil applied to the column was recovered on the soil. With the fully diluted SRS-FR, most of the oil was recovered at the top of the column (1,260 mg/kg) with between 720 and 810 mg/kg in the next three sections and only 20 mg/kg at the bottom. Approximately 664 mg of the

TABLE 1. Results of transport studies under gravity-flow conditions with partially and fully-diluted SRS-FR.

Treatment	Water (mL)	Emulsion (mL)	Volume of first emulsion appearance (mL)	Total recovered (mL)	Flow rate (mL/min)
Column 1—Four Aliquots of 10 mL SRS-FR + 40 mL Tap Water Chased with 138 mL Tap Water.					
1A	150			32	0.6
1B	150			138	5.7
1C	150			154	2.6
1D	150			166.5	2.1
1E		150	-	154	2.5
1F		150	135	144	3.5
1G		150	50	149	2.5
1H		150	-	142	2.5
Column 2—Three Aliquots of 8 mL SRS-FR + 492 mL Tap Water					
2A	150			43	0.7
2B	150			133	3.9
2C	150			153	3.5
2D	150			150	1.9
2E		150	-	53	0.7
2F		150	-	142	2.1
2G		150	-	145	2.5

TABLE 2. Oil distribution in soil under gravity-flow conditions with partially and fully-diluted SRS-FR

Sample	Interval	Oil conc. (mg/kg)	Mass Balance (mg)
Column 1 - 10 mL SRS-FR + 40 mL Tap Water Chased with 138 mL Tap Water.			
1S1	Top	440	81
1S2		280	52
1S3		580	107
1S4		140	26
1S5	Bottom	0	0
Total			266
Column 2 - 8 mL SRS-FR + 492 mL Tap Water			
2S1	Top	1260	233
2S2		810	150
2S3		720	133
2S4		780	144
2S5	Bottom	20	4
Total			664

13,248 mg of oil applied to this column was recovered from the soil. Under gravity flow conditions, the partially diluted SRS-FR followed by chase water moved farther through the soil column whereas the flow of the fully diluted SRS-FR was retarded.

Column Studies 2—Pumped Feed of SRS-FR. These column studies were repeated under pumped conditions. Soil columns were prepared with 1,200 g of DAFB soil. Tap water along with the emulsion solutions were introduced onto the soil columns in an up-flow mode at about 3 to 5 mL/min utilizing a peristaltic pump. Injection of two aliquots of concentrated moderate droplet size EVO (1 part EVO to 4 parts water) followed by chase water allowed for the visible transport of the emulsion to the column effluent after approximately 1.5 pore volumes (Table 3). The greatest quantity of hexane-extraction oil in the soil was found closest to the inlet with very little oil in the final (upper) segment (Table 4). A mass balance suggested that 3,947 mg of oil was retained on the soil out of the approximately 11,040 mg applied to the column. A second test conducted with the moderate particle size EVO (diluted 62.5 to 1) was not visibly detected in the column effluent after two applications of approximately 2.6 pore volumes. The greatest hexane-extractable oil concentrations in the soil were closest to the inlet with lower oil concentrations in the upper (last) segment suggesting that some oil was distributed throughout the column although it was not observed in the effluent. Essentially half of the oil was recovered from the column (4,411 mg recovered on the soil from the approximately 8,832 mg applied to the column). Once again, the partially diluted EVO moved through the soil column better than the fully diluted EVO.

Column Study 3—Pumped Small Droplet Size of SRS. Another set of columns tests were conducted with SRS, a smaller droplet size emulsion, amended with sodium chloride as a tracer. Effluent analysis included chloride tracer (specific conductivity), visual and microscopic observation of the emulsion, TOC, VFAs, and FAME a semi-quantitative esterification method followed by GC/FID detection). Soil samples were analyzed for hexane-extractable oil and FAME.

In the column with 4 parts water and 1 part SRS dilution followed by chase water; the emulsion and tracer were observed after about 1 pore volume. Lactate and TOC concentrations were detected at elevated levels in the effluent samples collected at about this time, but none of the FAME constituents were detected (Table 5). Low to medium levels of FAME were detected after 1.2 pore volumes. After 1.5 pore volumes, no VFA were detected and the tracer concentration had declined, yet the emulsion was still visible in the column. Low to high levels of FAME were found throughout the soil column. Hexane-extractable oil was only found near the inlet and the fourth section of the column (Table 6). A total of 7,414 mg of oil was recovered from the column. The mass balance was anomalous as only 5,520 mg of oil was applied to the column.

With the more diluted EVO (61.5 parts water to 1 part SRS), the emulsion also appeared after about 1 pore volume as the tracer and TOC were increasing. FAME didn't appear until 1.3 pore volumes, similar to column 1, but no VFAs were detected in the column effluent. The oil content in the soil from this column was low near the inlet and greater near the outlet. Once again, the mass balance was anomalous as only about 6,182 mg of oil was applied to the column.

TABLE 3. Results of transport studies under pumped-flow conditions with partially and fully-diluted SRS-FR.

Treatment	Emul. Vol. (mL)	Vol. first emul. appear. (mL)	Total recovered (mL)	Flow rate (mL/min)
10 mL SRS + 40 mL tap water	500	-	424	3.0
10 mL SRS + 40 mL tap water	500	100	476	3.4
8 mL SRS + 492 mL tap water	500	-	479	5.5
8 mL SRS + 492 mL tap water	500	-	451	5.0

TABLE 4. Oil distribution in soil under pumped-flow conditions with partially and fully-diluted SRS-FR.

Sample	Position	Oil Conc. (mg/kg wet wt)	Oil Mass Balance (mg)
Column 3 - Pumped 10 mL SRS-FR + 40 mL Tap Water + Chase Water			
S1	Inlet	5410	1298
S2		4900	1176
S3		2650	636
S4		3330	799
S5	Outlet	160	38
Total Column 1			3947
Column 4 - 8 mL SRS-FR + 492 mL Tap Water			
S1	Inlet	5620	1345
S2		3920	941
S3		3920	941
S4		3320	797
S5	Outlet	1600	384
Total Column 2			4411

TABLE 5. Results of transport studies under pumped-flow conditions with partially and fully-diluted SRS.

Column 1 - SRS Diluted 1:5 with Chase Water												
Vol. eff.(mL)	**Pore Vol.**	**Cond. (uS)**	**SRS Obs.**	**Microscope**	**TOC**	**Lactate**	**Palmitic**	**Stearic**	**Oleic**	**Linoleic**	**Arachidic**	**Linolenic**
50	0.12	456	No	No								
100	0.24	186	No	No								
150	0.37	139	No	No			* T					
175	0.43	113	No		78							
200	0.49	106	No	No								
250	0.61	353	No	No								
300	0.73	2240	No	No								
325	0.79	2580	No				* T					
350	0.85	3400	No	No		690						
400	0.98	3080	Yes	No								
425	1.04	3070	Yes	Yes	281							
450	1.10	2900	Yes	Yes								
475	1.16	2660	Yes				* M	* L	* M	* L		
500	1.22	2320	Yes	Yes								
550	1.34	1708	No	Yes	214							
600	1.46	1467	No	Yes		<25						
650	1.59	1353	Yes	Yes			* T	* T	* T			
675	1.65	1260	Yes									
Column 2 - SRS Diluted 61.5:1												
50	0.14	595	No	No								
100	0.27	171	No	No								
150	0.41	175	No				* L	* VL	* L	* L		* VL
175	0.48	395	No		50							
200	0.55	540	No	No								
250	0.68	845	No									
300	0.82	1060	No	No		<25						
350	0.96	1229	No	Yes	107							
400	1.10	1288	No	Yes			* T		* T	* T		
450	1.23	1136	No	Yes								
475	1.30	1361	Yes	Yes			* H	* M	* H	* T		
500	1.37	1428	Yes	Yes								
550	1.51	1470	Yes	Yes	184							
600	1.64	1611	Yes	Yes		<25						
650	1.78	1649	Yes				* H	* H	* H	* H	* VL	* H
675	1.85	1671	Yes	Yes								

*T = Trace * VL = Very Low *L = Low * M = Medium * H = High

TABLE 6. Oil and FAME distribution in soil under pumped-flow conditions with partially and fully-diluted SRS.

Soil		Hexane Extractable Oil mg/kg	Palmitic	Stearic	Oleic	Linoleic	Arachidic	Linolenic
Column 1 - SRS 10 mL SRS with 40 mL Water Followed by 650 mL Chase Water								
5	Inlet	2,796	* L	* VL	* L	* L		* VL
4		0	* M	* L	* L	*M		* VL
3		0	* H	* L	* M	* H	* T	* L
2		4,618	* M	* L	* M	* H	* T	* L
1	Outlet	0	* H	* L	* L	* L	* T	* L
	Total	7,414						
Column 2 - SRS 11.2 mL SRS Diluted with 668.8 mL Water								
5	Inlet	2,218	* H	* M	* H	* H	* T	* L
4		2,663	* H	* M	* H	* H	* T	* L
3		4,478	* H	* M	* H	* H	* T	* L
2		2,205	* H	* H	* H	* H	* L	* L
1	Outlet	0	* M	* M	* H	* H	* T	* L
	Total	11,564						

* T = Trace * VL = Very Low * L = Low * M = Medium * H = High

CONCLUSIONS

In conclusion, injection of a 1 part EVO and 4 parts water mixture followed by chase water allowed for greater transport of the emulsion than injection of the more diluted EVO. The finer droplet size formulation moved through the soil column easier than the larger droplet size EVO, thus providing better distribution throughout the formation. EVO was detected in the effluent of the soil columns only after about one pore volume of the SRS or SRS-FR. FAME analysis of water samples proved useful in determining the presence of vegetable oil whereas TOC also measures the presence of lactate. Hexane-extraction and FAME analysis served as useful methods in determining the presence of vegetable oil in soil samples.

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EMULSIFED VEGETABLE OIL TRANSPORT STUDIES IN SOIL COLUMNS

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OVERVIEW

- EVO PROPERTIES
- METHODS
- RESULTS OF EVO DISTRIBUTION
- CONCLUSIONS
- FRACTURED BEDROCK EVO

EVO PROPERTIES

- 45 TO 60% OIL, FOOD GRADE SURFACTANTS, SODIUM LACTATE, AND NUTRIENTS
- AVERAGE DROPLET SIZE <1 & 5 MICRONS
- OIL DROPLETS TRANSPORTED THROUGH SOIL INITIALLY
- EMULSION BREAKS
- RESIDUAL OIL LAYER IS SLOWLY BIODEGRADED

EVO DISTRIBUTION

EVO INJECTED BY DIRECT PUSH OR INTO WELLS

- TYPICALLY FULLY DILUTED (1 TO 100 TIMES)
- PARTIALLY DILUTED (1 TO 5 TIMES EVO) AND FOLLOWED BY CHASE WATER
- CHASE WATER EITHER TAP OR RECIRCULATED GROUNDWATER
- INCREASED TRANSPORT REDUCES COSTS FOR INJECTION

DOVER AIR FORCE BASE COLUMN STUDIES

Terra Systems
INCORPORATED

METHODS

- COLUMNS (925 TO 1,200 G) PREPARED WITH DOVER AFB SOILS – FINE TO MEDIUM GRAINED SAND
- GRAVITY DOWNFLOW OR PUMPED UPFLOW
- MONITORED
  - VISUAL APPEARANCE
  - MICROSCOPIC DROPLET SIZE
  - SPECIFIC CONDUCTIVITY
  - TOC AND COD
  - VOLATILE ACIDS
  - FATTY ACID METYL ESTERS
  - HEXANE EXTRACTION OF SOIL SAMPLES

COLUMN STUDY 1

- 925 G SOIL
- GRAVITY FEED FROM TOP
- 1 PORE VOLUME ~300 ML
- PARTIALLY DILUTED LD EVO (1 PART EVO TO 4 PARTS WATER) FOLLOWED BY CHASE WATER
- FULLY DILUTED LD EVO (1 PART EVO TO 61.5 PARTS WATER)
- MONITORED
  - VISUAL
  - FLOW RATE
  - SOIL HEXANE EXTRACTABLE OIL

COLUMN STUDY 1
GRAVITY FEED OF LARGE DROPLET SIZE EVO

Column 1- Four Aliquots of 1:4 Diluted LD EVO Chased with Tap Water. 1 PV = 300 mL

Treatment	Water (mL)	Emul-sion (mL)	First emul-sion (mL)	Flow rate (mL/min)
1A	150			0.6
1B	150			5.7
1C	150			2.6
1D	150			2.1
1E		150	-	2.5
1F		150	135	3.5
1G		150	50	2.5
1H		150	-	2.5

Column 2 - Three Aliquots of 1:61.5 LD EVO to Tap Water. 1 PV = 300 mL

Treatment	Water (mL)	Emul-sion (mL)	First emul-sion (mL)	Flow rate (mL/min)
2A	150			0.7
2B	150			3.9
2C	150			3.5
2D	150			1.9
2E		150	-	0.7
2F		150	-	2.1
2G		150	-	2.5

COLUMN STUDY 1
GRAVITY FEED OF LARGE DROPLET SIZE EVO HEXANE EXTRACTABLE OIL

Column 1- Four Aliquots of 1:4 Diluted LD EVO Chased with Tap Water. 1 PV = 300 mL

Sam-ple	Interval	Oil conc. (mg/kg)	Mass Balance (mg)
1S1	Top	440	81
1S2		280	52
1S3		580	107
1S4		140	26
1S5	Bottom	0	0
Total			266/ 4000

Column 2 - Three Aliquots of 1:61.5 LD EVO to Tap Water. 1 PV = 300 mL

Sample	Interval	Oil conc. (mg/kg)	Mass Balance (mg)
2S1	Top	1260	233
2S2		810	150
2S3		720	133
2S4		780	144
2S5	Bottom	20	4
Total			664/ 4000

COLUMN STUDY 2

- 1200 G SOIL
- PUMPED FROM BOTTOM
- ONE PORE VOLUME ~385 ML
- PARTIALLY DILUTED LD EVO (1 PART EVO TO 4 PARTS WATER) FOLLOWED BY CHASE WATER
- FULLY DILUTED LD EVO (1 PART EVO TO 61.5 PARTS WATER)
- MONITORED
  - VISUAL
  - FLOW RATE
  - SOIL HEXANE EXTRACTABLE OIL

COLUMN STUDY 2
PUMPED FEED OF LARGE DROPLET SIZE EVO

LD EVO DILUTED 1:4 WITH CHASE WATER

Emulsion Volume (mL)	First emulsion (mL)	Flow rate (mL/min)
500	-	3.0
500	100	3.4

LD EVO DILUTED 1:61.5

Emulsion Volume (mL)	First emulsion (mL)	Flow rate (mL/min)
500	-	5.5
500	-	5.0

COLUMN STUDY 2
PUMPED FEED OF LARGE DROPLET SIZE EVO HEXANE EXTRACTABLE OIL

Column 1- 2 Aliquots of 1:4 Diluted LD EVO Chased with Tap Water.

1 PV = 385 mL

Sam-ple	Interval	Oil conc. (mg/kg)	Mass Balance (mg)
S1	Inlet	5410	1298
S2		4900	1176
S3		2650	636
S4		3330	799
S5	Outlet	160	38
Total			3947/ 11040

Column 2 - Three Aliquots of 1 Part EVO to 61.5 Parts Tap Water.

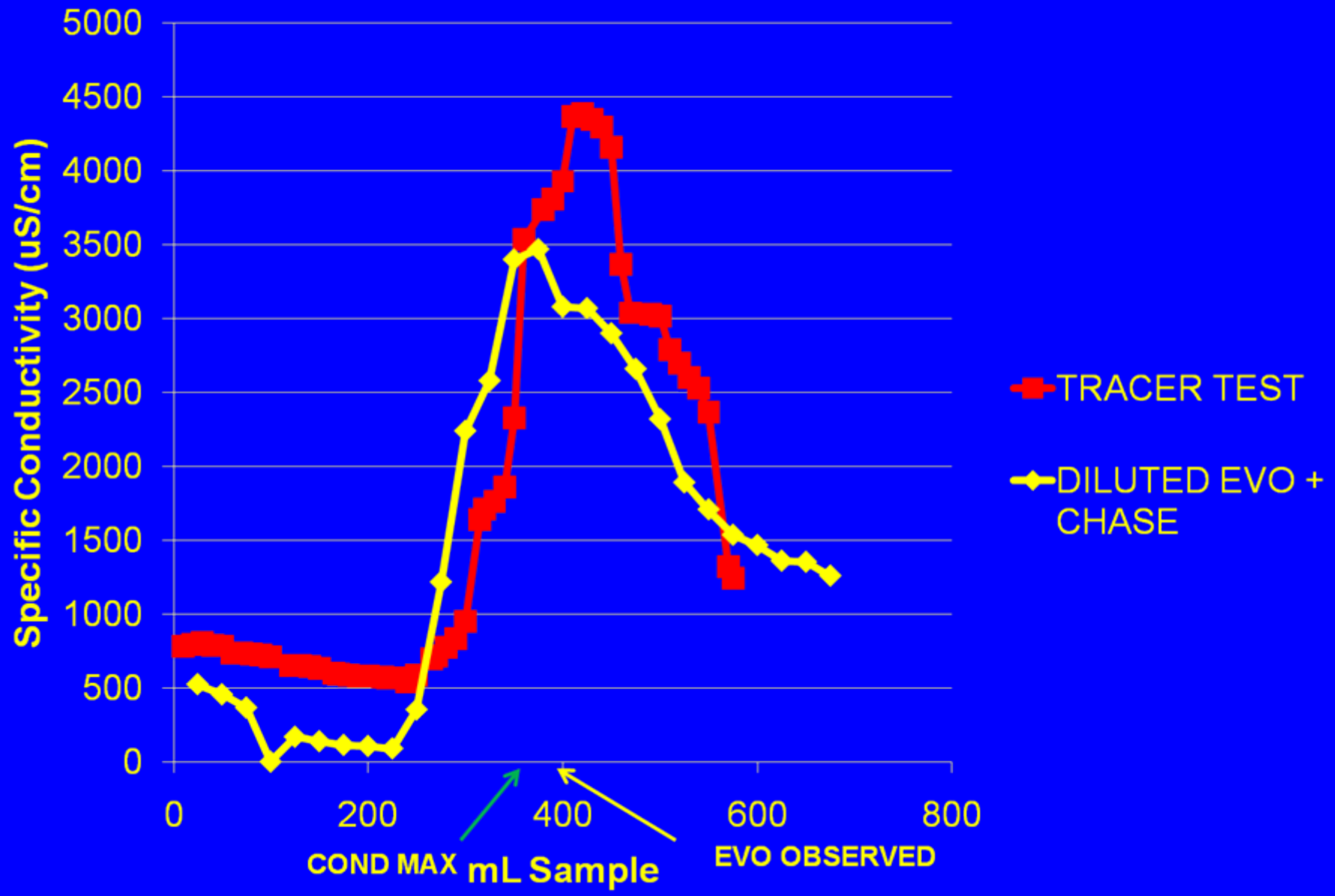
1 PV = 385 mL

Sample	Interval	Oil conc. (mg/kg)	Mass Balance (mg)
S1	Inlet	5620	1345
S2		3920	941
S3		3920	941
S4		3320	797
S5	Outlet	1600	384
Total			4411/ 8830

COLUMN STUDY 3

- 1200 G SOIL
- PUMPED FROM BOTTOM
- ONE PORE VOLUME ~385 ML
- SMALL DROPLET SIZE (AVERAGE OF 0.4 UM)
- PARTIALLY DILUTED SD EVO (1 PART EVO TO 4 PARTS WATER) FOLLOWED BY CHASE WATER
- FULLY DILUTED SD EVO (1 PART EVO TO 61.5 PARTS WATER)
- MONITORED
  - VISUAL AND MICROCOSCOPIC
  - SPECIFIC CONDUCTIVITY
  - TOC
  - VFAS
  - FAME
  - SOIL HEXANE EXTRACTABLE OIL AND FAME

PARTIALLY DILUTED SD EVO + CHASE



Terra Systems INCORPORATED

COLUMN STUDY 3 PUMPED-FLOW CONDITIONS WITH PARTIALLY DILUTED SD EVO FOLLOWED BY CHASE WATER

Vol. eff.(mL)	Pore Vol.	Cond. (uS)	EVO Obs.	Micro-scope	TOC	Lac-tate	Palm-itic	Stea-ric	Ole-ic	Lino-leic	Arach-idic	Lino-lenic
50	0.12	456	No	No								
100	0.24	186	No	No								
150	0.37	139	No	No			* T					
175	0.43	113	No		78							
200	0.49	106	No	No								
250	0.61	353	No	No								
300	0.73	2240	No	No								
325	0.79	2580	No				* T					
350	0.85	3400	No	No		690						
400	0.98	3080	Yes	No								
425	1.04	3070	Yes	Yes	281							
450	1.10	2900	Yes	Yes								
475	1.16	2660	Yes				* M	* L	* M	* L		
500	1.22	2320	Yes	Yes								
550	1.34	1708	No	Yes	214							
600	1.46	1467	No	Yes		<25						
650	1.59	1353	Yes	Yes			* T	* T	* T			
675	1.65	1260	Yes									

COLUMN 3 PUMPED-FLOW CONDITIONS WITH FULLY DILUTED SD EVO

Vol. eff.(mL)	Pore Vol.	Cond. (uS)	SRS Obs.	Micros-cope	TOC	Lac-tate	Palm -itic	Stea-ric	Oleic	Lino-leic	Arac h-idic	Lino-lenic
50	0.14	595	No	No								
100	0.27	171	No	No								
150	0.41	175	No				* L	* VL	* L	* L		* VL
175	0.48	395	No		50							
200	0.55	540	No	No								
250	0.68	845	No									
300	0.82	1060	No	No		<25						
350	0.96	1229	No	Yes	107							
400	1.10	1288	No	Yes			* T		* T	* T		
450	1.23	1136	No	Yes								
475	1.30	1361	Yes	Yes			* H	* M	* H	* T		
500	1.37	1428	Yes	Yes								
550	1.51	1470	Yes	Yes	184							
600	1.64	1611	Yes	Yes		<25						
650	1.78	1649	Yes				* H	* H	* H	* H	* VL	* H
675	1.85	1671	Yes	Yes								

COLUMN STUDY 3
SMALL DROPLET EVO SOIL SAMPLES

SOIL		HEXANE EXTRACT-ABLE OIL MG/KG	MASS BAL-ANCE	PALMI-TIC	STEARIC	OLEIC	LINO-LEIC	ARACHI-DIC	LINO-LENIC
PARTIALLY DILUTED EVO 1:4 FOLLOWED BY CHASE WATER									
5	Inlet	2,796	671	* L	* VL	* L	* L		* VL
4		0	0	* M	* L	* L	*M		* VL
3		0	0	* H	* L	* M	* H	* T	* L
2		4,618	1108	* M	* L	* M	* H	* T	* L
1	Outlet	0	0	* H	* L	* L	* L	* T	* L
	Total		1179/ 11040						
FULLY DILUTED EVO 1:61.5									
5	Inlet	2,218	532	* H	* M	* H	* H	* T	* L
4		2,663	639	* H	* M	* H	* H	* T	* L
3		4,478	1075	* H	* M	* H	* H	* T	* L
2		2,205	529	* H	* H	* H	* H	* L	* L
1	Outlet	0	0	* M	* M	* H	* H	* T	* L
			2775/ 8832						

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CONCLUSIONS

- INJECTION OF PARTIALLY DILUTED EVO FOLLOWED BY CHASE WATER RESULTED IN GREATER TRANSPORT THAN FULLY DILUTED EVO
- SMALLER DROPLETS GAVE BETTER TRANSPORT THAN LARGER DROPLETS
- EVO DETECTED IN EFFLUENT AFTER ONE PORE VOLUME
- FAME ANALYSIS USEFUL TO MONITOR EVO
- TOC MEASURES LACTATE AND SURFACTANTS ALSO
- HEXANE EXTRACTION AND FAME USEFUL FOR DETERMINING PRESENCE OF EVO IN SOILS

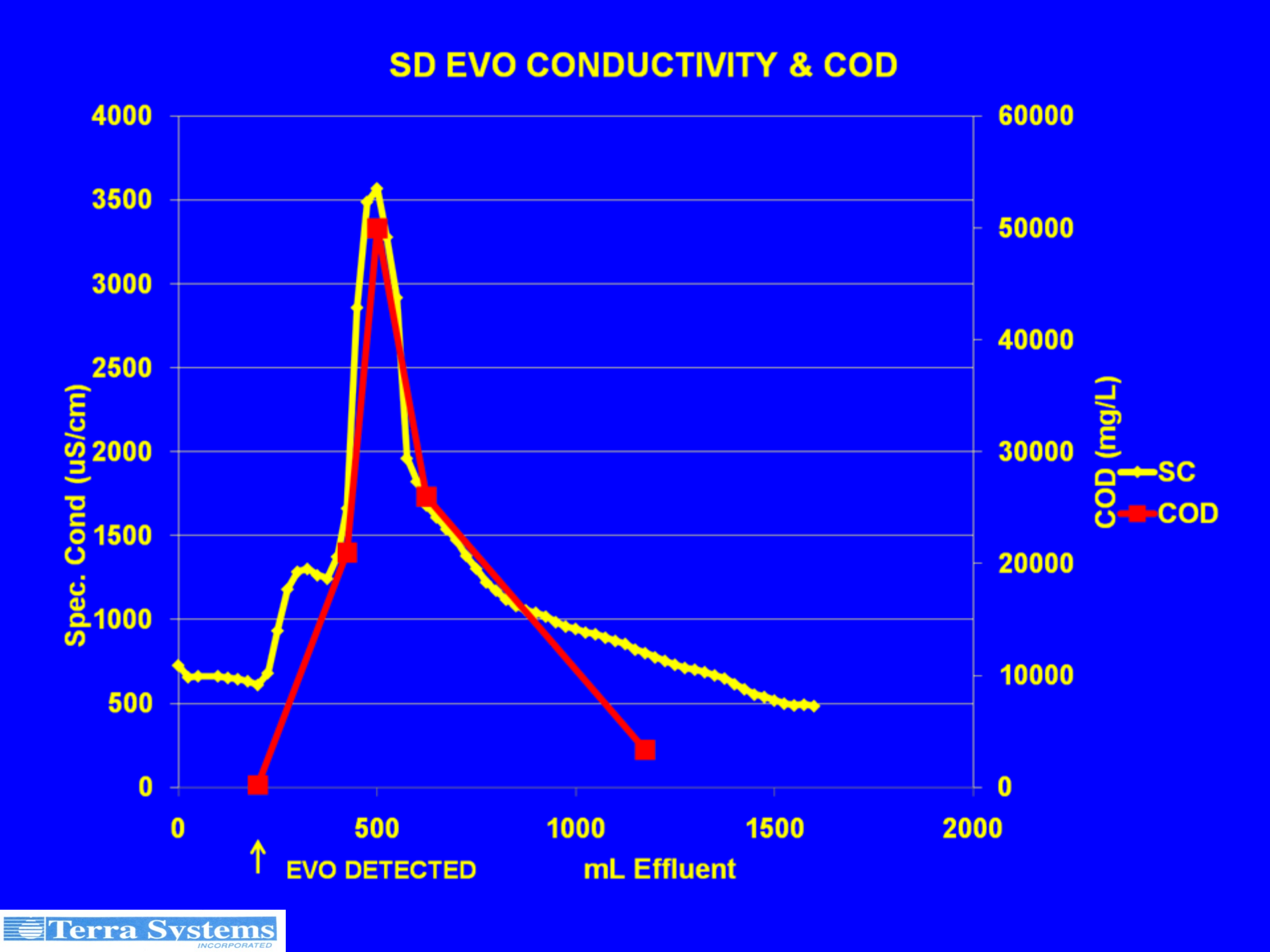
FRACTURED ROCK COLUMN STUDIES

- GOAL IS TO INCREASE EVO RETENTION ONTO FRACTURED ROCK TO PROVIDE ENOUGH CARBON AND REDUCE MIGRATION AWAY FROM SOURCE AREA
- INCREASE DROPLET SIZE TO GET BETTER RETENTION
- ALTER EVO FOR IMPROVED RETENTION

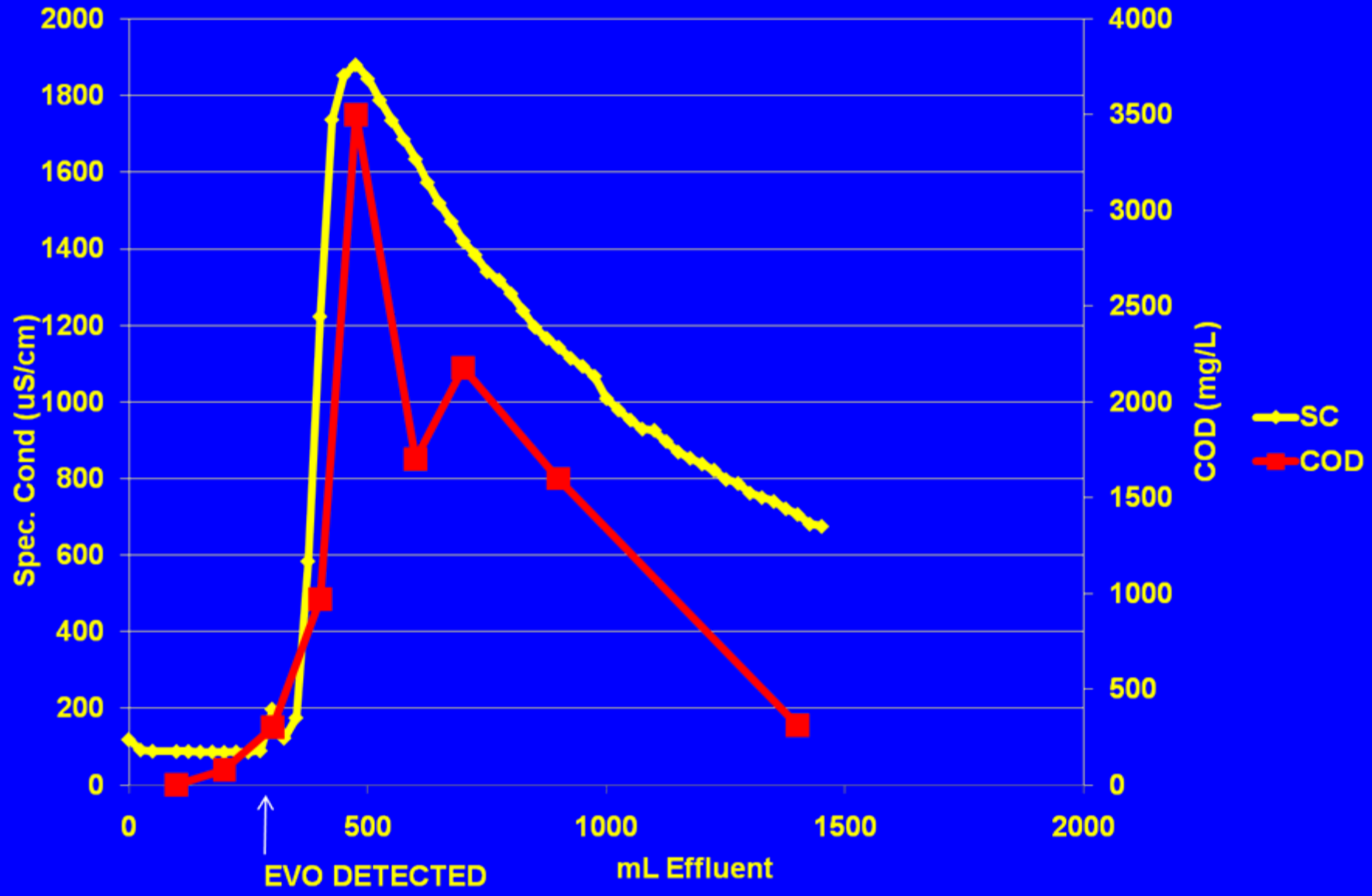
FRACTURED ROCK COLUMN STUDIES

- COLUMNS PREPARED WITH 1.4 KG PEA GRAVEL
- 24 TO 29% POROSITY
- COMPARED PARTIALLY DILUTED SD EVO (MEAN 0.6 μM) WITH PARTIALLY DILUTED LD EVO (MEAN 3.8 μM)
- MONITORED
  - SPECIFIC CONDUCTIVITY
  - VISUAL APPEARANCE
  - COD
  - HEXANE EXTRACTABLE OIL

FRACTURED ROCK TRANSPORT



FRACTURED ROCK LD EVO CONDUCTIVITY AND COD



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COLUMN STUDY 4 FRACTURED ROCK PUMPED FEED OF SD AND LD EVO HEXANE EXTRACTABLE OIL

1:4 DILUTED SD EVO + CHASE WATER 1 PV = 390 mL

Sam-ple	Interval	Oil conc. (mg/kg)	Mass Balance (mg)
S1	Inlet	20	5.4
S2		145	39.4
S3		0	0
S4		480	130.6
S5	Outlet	5	1.4
Total			176.8/ 5520

1:4 DILUTED LD EVO + CHASE WATER 1 PV = 340 mL

Sample	Interval	Oil conc. (mg/kg)	Mass Balance (mg)
S1	Inlet	1328	378
S2		451	128
S3		1085	309
S4		50	14
S5	Outlet	696	198
Total			1029/ 5520

FRACTURED ROCK CONCLUSIONS

- REDUCED TRANSPORT FOR FR EVO VS SMALL DROPLET EVO
- MORE EVO RETENTION ON SOIL MATRIX