ENVIRONMENT AGENCY

WATER QUALITY SECTION
CORNWALL AREA

FINAL DRAFT REPORT

RIVER TAMAR
ANNEX 1A INVESTIGATION

November 1996
COR/96/010
Author: Rob Hocking
Investigations Technician

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Area Manager

EA-South West / 99-15
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RIVER TAMAR ANNEX 1A INVESTIGATION

1. INTRODUCTION

1.1 Background

At the second and third North Sea Conferences in 1987 and 1990, the UK Government made a commitment to reduce the loads (load = concentration x flow) of certain substances, known as Annex 1A substances, entering tidal waters from rivers and direct discharges. Annex 1A substances are those which are toxic, persistent and/or bioaccumulative.

Since 1991 loadings of Annex 1A substances have been detected in the River Tamar at the harmonised monitoring site at Gunnislake Bridge (R12E003). The routine monitoring data shows there are sources throughout the Tamar catchment. Holsworthy (Derriton) Sewage Treatment Works (STW) and Launceston (St.Leonards) STW are known to be point sources but in low concentrations. Figure 1 shows the River Tamar freshwater catchment identifying the Gunnislake Bridge site, STW's, the sampling points and gauging stations used in the investigation.

Data from Gunnislake Bridge is collected for the routine monitoring program, Annex 1A and Paris Commission purposes. The data collected since 1991 has shown significant loadings of the following substances: The insecticide Gamma HCH detected in 1991,1992 and 1993, the herbicide Trifluralin detected in 1992, Dieldrin detected in 1992, HCB in 1993 and Organotins in 1993.

1.2 Objectives

To identify sources of Annex 1A substances in the Tamar catchment that are contributing to the significant loadings at Gunnislake Bridge.

2. METHODS

i) Four chemical surveys were conducted in late 1995 and early 1996. Samples were taken from routine monitoring points in the Tamar catchment. Two of the surveys were included with the routine Tamar sampling run.

ii) One set of samples were taken from two separate farm dirty water systems to identify possible sources of Annex 1A substances.

iii) After two chemical surveys had been conducted discussions were held between Cornwall Area Water Quality Team (East) and the Investigations Team to review the data collected and to adjust the sampling required.

v) All results from the chemical surveys were tabulated with flow data to calculate loadings.

3. RESULTS

Sampling sites and gauging stations are shown in figure 1. Summaries of the four chemical surveys conducted are shown in Tables 1 to 4. Where gaps are present in the tables, concentrations were below detection limits. Results from the two samples taken from farm dirty water systems are shown in appendix 1 and 2.

Attention should be drawn to the organotin data from the survey conducted on 19 March 1996. Initial results showed higher levels of organotins, when queried the laboratory admitted that problems had occurred with the organotin analysis and the sample results were adjusted in the laboratory by blank correcting (see Appendix 3). The organotin results shown are still not consistent with those from archived data and previous surveys conducted within this investigation. The results show concentrations of organotins throughout the Tamar catchment, with no known sources and no patterns. The laboratory are not confident as to the reliability of these results. Organotin analysis methodology has now changed preventing the possibility of further mistakes.

4. DISCUSSIONS

From the four chemical samples taken from Gunnislake Bridge during this investigation only two of them detected Annex 1A substances. The pesticide compound detected and the one most frequently found in the Tamar catchment was Gamma HCH. It was detected in 50% of the samples taken for this investigation. The agricultural industry use pesticides containing Gamma HCH in many farming practices. It is used to control pests in livestock houses, on field crops, vegetables, fruit and in forestry plantations and nursery beds. However, concentrations were low indicating a widespread diffuse input of Gamma HCH.

Gunnislake Bridge at R12E003 (site Z) is a background monitoring site for the EC Dangerous Substance Directive. The Environmental Quality Standard (EQS) for the EC Dangerous Substance Directive at a background monitoring site for Gamma HCH is a maximum concentration of 50 ng/l taken over an annual average. Concentrations of Gamma HCH detected at this site were well within these limits.

The Colesmill Stream downstream of Holsworthy STW (site F) is a designated Dangerous Substance site for Gamma HCH. The (EQS) for the EC Dangerous Substance Directive for Gamma HCH is set at a maximum allowable concentration of 100 ng/l taken as an annual average. The Freshwater Tamar and Tributaries Catchment Management Plan Consultation Report written in 1995 states, 'The Environmental Quality Standards for List 1 Dangerous Substances have been met at all sites monitored in the catchment since 1991'.

The two samples taken from farm dirty water systems in the Tamar catchment show low concentrations of Annex 1A substances but not sufficient quantities as to affect the River Tamar.

The results from the Annex 1A and Paris Commission surveys show significant loadings of organochlorines and organotins at Gunnislake Bridge but also show that the concentrations are low in comparison to EQS for the EC Dangerous Substance Directive. Sewage treatment works were the only point sources where Annex 1A substances were consistently detected. Concentrations downstream of the STW's are well within EQS for EC Dangerous Substance Directive.

5. CONCLUSIONS

i) Annex 1A substances are found irregularly throughout the River Tamar catchment in low concentrations.

ii) Annex 1A substances are found more regularly during lower flow conditions.

iii) Sewage Treatment Works are confirmed to be point sources but in low concentrations.

iv) Gamma HCH which is widely used in agriculture is the most common Annex 1A pesticide to be found in the Tamar catchment.

6. RECOMMENDATIONS

i) Include organochlorine and organotin sampling to the Farm Waste Management Study on the Smallbrook, a tributary of the main River Tamar. This intense study could identify possible pathways of Annex 1A substances in a typical tributary catchment of the River Tamar.

Action - Bruce Newport

ii) Further investigation work should be carried out with South West Water PLC to identify pathways of Annex 1A substances to STW. Chemical and flow data should be collected from sewage influents, storm water overflows and final effluents to calculate loadings of Annex 1A substances.

Action - Bruce Newport

Reference:
Freshwater and Tributaries Catchment Management Plan Consultation Report. National River Authority South Western Region 1995.

TABLE 1.TAMAR CATCHMENT: ORGANOCHLORINES AND ORGANOTINS DETECTED ON 1st NOVEMBER 1995

SITE	SITE	URN	FLOW	HCH GAMMA		HCH ALPHA		HCH BETA		DIELDRIN	
			M3/ DAY	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	oading (g/year)	Conc. (ng/l)	oading (g/year	Conc. (ng/l)	Loading (g/year)
Upper Tamar Resv. at Dam	A	R12L030		1.6							
Tamar at Crowford Bridge	C	R12L003	42094.0	1.0	15.364						
Holsworthy STW Final Effluent	D	WSTW3139FE		11.0		2.9				2.1	
Colesmill Stm Upstream of Holsworthy STW	E	WSTW3139A		1.0							
Colesmill Stm Downstream of Holsworthy STW	F	R12K007		2.9				0.8			
Deer at Deer Bridge	G	R12K005		1.7							
River Claw at Tetcott Bridge	H	R12K002		1.4							
Tamar at Netherbridge	I	R12J003		1.2				0.4			
Tamar at Polson Bridge	J	R12J004	173287.0	1.7	107.525						
Tamar Upstream of St.Leonards	K	WSTW4644A		2.0		0.3		2.4			
St.Leonards STW FE	L	WSTW4644FE		SAMPLE		LOST		IN		LAB	
Tamar at Greystone Bridge	M	R12E001		1.2							
Inny at Beals Mill Bridge	N	R12P006	123729.0	0.9	40.645						
Wolf at Weeks Mill Bridge	O	R12G005	6195.0	0.5	1.131						
Hennard Stream	P	R12G096	2884.0	<0.5							
Wolf at Roadford Newbridge	Q	R12G084	46348.0	3.9	65.976	0.5	8.459	0.5	8.459		
Thrushel at Tinhay Bridge	R	R12G004	77825.0	2.6	73.856	0.4		0.4			
River Lew Upstream of the Lyd	S	R12F004		0.6							
River Lyd Upstream of the Thrushel	T	R12F016		0.5							
Lyd at Lifton Bridge	U	R12F002	186525.0	1.4	95.314						
Carey at Heale Bridge	V	R12H002		1.0							
Ottery at Ham Mill Bridge	W	R12M007	42005.0								
River Kensay at St.Leonards Bridge	X	R12N002		1.4							
Gunnislake Surface Water Abstraction Point	Y	R12E035		1.1							
Tamar at Gunnislake Bridge	Z	R12E003	573999.0	1.4	293.313						

Where no data is present concentrations are below detection limits.

TABLE 2.TAMAR CATCHMENT: ORGANOCHLORINES AND ORGANOTINS DETECTED ON 6th DECEMBER 1995

SITE	SITE	URN	FLOW	HCH GAMMA		HCH ALPHA		DIELDRIN		TRIPHENYL TIN		TETRABUTYL TIN		MONOBUTYL TIN		TRIBUTYL TIN	
			M3/ DAY	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)
Upper Tamar Resv. at Dam	A	R12L030		0.9		0.3				679.0		535.0					
Tamar at Crowford Bridge	C	R12L003	126748.8	0.8	37.0												
Holsworthy STW Final Effluent	D	WSTW3139FE		140.0		0.4		0.8						76.0			
Colesmill Stm Upstream of Holsworthy STW	E	WSTW3139A		<0.5													
Colesmill Stm Downstream of Holsworthy STW	F	R12K007		9.3													
Deer at Deer Bridge	G	R12K005															
River Claw at Tetcott Bridge	H	R12K002														20.0	
Tamar at Netherbridge	I	R12J003		0.7												14.0	
Tamar at Polson Bridge	J	R12J004	792460.8	1.2	347.1												
Tamar Upstream of St Leonards	K	WSTW4644A															
St Leonards STW FE	L	WSTW4644FE		16.7				2.1									
Tamar at Greystone Bridge	M	R12E001		0.6													
Inny at Beals Mill Bridge	N	R12P006															
Wolf at Weeks Mill Bridge	O	R12G005															
Hennard Stream	P	R12G096															
Wolf at Roadford Newbridge	Q	R12G084	10195.2	2.6	9.7	0.4	1.5										
Thrushel at Tinhay Bridge	R	R12G004															
River Lew Upstream of the Lyd	S	R12F004															
River Lyd Upstream of the Thrushel	T	R12F015															
Lyd at Lifton Bridge	U	R12F002															
Carey at Heale Bridge	V	R12H002															
Ottery at Ham Mill Bridge	W	R12M007															
River Kensay at St Leonards Bridge	X	R12N002															
Gunnislake Surface Water Abstraction Point	Y	R12E035															
Tamar at Gunnislake Bridge	Z	R12E003															

Where no data is present concentrations are below detection limits.

TABLE 3.TAMAR CATCHMENT: ORGANOCHLORINES AND ORGANOTINS DETECTED ON 14th FEBRUARY 1996

SITE	SITE	URN	FLOW	HCH GAMMA		HCH ALPHA		DIELDRIN		TRIPHENYL TIN		TRIBUTYL TIN		DDT (OP')	
			M3/ DAY	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)
Upper Tamar Resv. at Dam	A	R12L030		0.8											
Bridgerule STW Final Effluent	B	WSTW3044FE		210.0				4.3							
Tamar at Crowford Bridge	C	R12L003	177946												
Holsworthy STW Final Effluent	D	WSTW3139FE				0.8								3.3	
Colesmill Stm Upstream of Holsworthy STW	E	WSTW3139A													
Colesmill Stm Downstream of Holsworthy STW	F	R12K007				0.5									
Deer at Deer Bridge	G	R12K005								178.0					
River Claw at Tetcott Bridge	H	R12K002													
Tamar at Netherbridge	I	R12J003													
Tamar at Polson Bridge	J	R12J004	1346067												
Tamar Upstream of St.Leonards	K	WSTW4644A													
St.Leonards STW FE	L	WSTW4644FE		10.0		0.9		3.1				23.0			
Tamar at Greystone Bridge	M	R12E001													
Inny at Beals Mill Bridge	N	R12P006	676920												
Wolf at Weeks Mill Bridge	O	R12G005	29800												
Hennard Stream	P	R12G096	18367												
Wolf at Roadford Newbridge	Q	R12G084	10294	1.6	6.01										
Thrushel at Tinhay Bridge	R	R12G004	220412												
River Lew Upstream of the Lyd	S	R12F004													
River Lyd Upstream of the Thrushel	T	R12F016													
Lyd at Lifton Bridge	U	R12F002	690064												
Carey at Heale Bridge	V	R12H002													
Ottery at Ham Mill Bridge	W	R12M007	406992												
River Kensay at St.Leonards Bridge	X	R12N002													
Gunnislake Surface Water Abstraction Point	Y	R12E035													
Tamar at Gunnislake Bridge	Z	R12E003	3353612												

Where no data is present concentrations are below detection limits.

TABLE 4.TAMAR CATCHMENT: ORGANOCHLORINES AND ORGANOTINS DETECTED ON 19th MARCH 1996

SITE NAME	SITE	URN	FLOW	HCH GAMMA		HCH ALPHA		DIELDRIN		TRIPHENYL TIN		TRIBUTYL TIN		TETRABUTYL TIN	
			M3/ DAY	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)	Conc. (ng/l)	Loading (g/year)
Upper Tamar Resv. at Dam	A	R12L030										19.2		54.1	
Bridgerule STW Final Effluent	B	WSTW3044FE		19.7		1.0		3.5				24.1		51.0	
Tamar at Crowford Bridge	C	R12L003	35471	0.8	10.36							20.8	269.30	61.7	798.82
Holsworthy STW Final Effluent	D	WSTW3135FE		14.1		2.1		1.1				22.6		65.6	
Colesmill Stm Upstream of Holsworthy STW	E	WSTW3139A								16.5		29.0		89.6	
Colesmill Stm Downstream of Holsworthy STW	F	R12K007		2.2		0.4				40.6		26.1		73.2	
Deer at Deer Bridge	G	R12K005		1.0								15.5		47.4	
River Claw at Tetcott Bridge	H	R12K002		1.2								27.4		81.3	
Tamar at Netherbridge	I	R12J003		0.9								42.0		55.0	
Tamar at Polson Bridge	J	R12J004	302010	0.7	77.16							26.0	2866.07		
Tamar Upstream of St.Leonards	K	WSTW4644A		0.8								107.0			
St Leonards STW FE	L	WSTW4644FE		20.3		2.4		2.8				34.2		85.5	
Tamar at Greystone Bridge	M	R12E001		0.7											
Inny at Beals Mill Bridge	N	R12P008	144011							27.0	1419.23	129.0	6780.76		
Wolf at Weeks Mill Bridge	O	R12G005	10083							26.0	95.69	93.0	342.27		
Hennard Stream	P	R12G096	5878							17.0	36.47	56.0	120.15		
Wolf at Roadford Newbridge	Q	R12G084	4562	1.5	2.50							42.0	69.94		
Thrushel at Tinhay Bridge	R	R12G004	78294	0.6	17.15					19.0	542.97	263.0	7515.83		
River Lew Upstream of the Lyd	S	R12F004								25.0		293.0			
River Lyd Upstream of the Thrushel	T	R12F016								63.0		54.0			
Lyd at Litton Bridge	U	R12F002	224433	0.6	49.15							106.0	8683.31		
Carey at Heale Bridge	V	R12H002		0.6								29.0		76.8	
Ottery at Ham Mill Bridge	W	R12M007	95073	0.7	24.29							29.5	1023.70	67.5	2342.36
River Kensay at St.Leonards Bridge	X	R12N002		0.7										60.4	
Gunnislake Surface Water Abstraction Point	Y	R12E035		0.6								23.5		65.4	
Tamar at Gunnislake Bridge	Z	R12E003	839316	1.0	308.35							16.2	4962.88	49.5	15164.34

Where no data is present concentrations are below detection limits.

Figure 1 - Freshwater Tamar Catchment

Information correct as of April 1995

Sample Analysis Run Report 19-MAR-96

Laboratory Ref. : E533526 Sampling Point : RPL/12L
Date/Time Taken : 19-MAR-96 13:20 Date/Time Received : 20-MAR-96 06:25
Pollution Incidents In Catchment 121

Address : Badharlick

Det.	Code	Description	Result
	3081	Isodrin total	< 0.9000 ng/l
*	3082	Hexachloro-Benzene total	< 0.6000 ng/l
*	3083	Hexachloro-Butadiene Total	< 2.5000 ng/l
	3142	PCB No.28	< 1.1000 ng/l
	3145	PCB No.52	< 4.3000 ng/l
*	3148	PCB No.101	< 1.2000 ng/l
	3151	PCB No.118	< 1.0000 ng/l
	3154	PCB No.138	< 0.9000 ng/l
*	3157	PCB No.153	< 1.4000 ng/l
*	3160	PCB No.180	< 1.3000 ng/l
	3270	1 2 3-Trichloro-Benzene	< 3.9000 ng/l
	3271	1 2 4-Trichloro-Benzene	< 22.9000 ng/l
*	3273	1 3 5-Trichloro-Benzene	11.6000 ng/l
	3276	Aldrin	< 0.4000 ng/l
	3294	DDE-(PP')	< 0.3000 ng/l
*	3295	DDE-(OP')	< 0.5000 ng/l
*	3296	DDT (OP')	< 2.5000 ng/l
	3297	DDT (PP')	< 0.3000 ng/l
	3301	Dieldrin	< 0.5000 ng/l
*	3303	Endosulphan A	< 0.5000 ng/l
	3304	Endosulphan B	< 1.7000 ng/l
	3306	Endrin	< 0.9000 ng/l
*	3310	HCH Alpha	< 0.3000 ng/l
*	3311	HCH Beta	8.1000 ng/l
	3312	HCH Delta	< 0.8000 ng/l
	3313	HCH Gamma	< 0.4000 ng/l
*	3329	TDE (OP')	< 1.5000 ng/l
	3330	TDE (PP')	< 0.5000 ng/l
	3335	Trifluralin	< 9.9000 ng/l
	3375	Organochlorine pesticide preparation	1.0000 Misc
*	3737	PCB No 31	< 1.4000 ng/l
	3738	PCB No 105	< 1.3000 ng/l
	3739	PCB No 156	< 1.6000 ng/l

'*' Indicates that Laboratory Determination Method is NAMAS Accredited.

APPENDIX 1

MENSAR V2.0.5
ENVIRONMENT AGENCY NLS EXETER LABORATORY

Sample Analysis Run Report 19-MAR-96

Laboratory Ref. : E533525 Sampling Point : RPL/12L
Date/Time Taken : 19-MAR-96 12:15 Date/Time Received : 20-MAR-96 06:25
Pollution Incidents In Catchment 121

Address : Merrifield

Sampler's Comments :
Dirty Water From System At Merrifield

Det.	Code	Description	Result
*3081		Isodrin total	< 0.9000 ng/l
*3082		Hexachloro-Benzene total	< 0.6000 ng/l
*3083		Hexachloro-Butadiene Total	< 2.5000 ng/l
*3142		PCB No.28	< 1.2000 ng/l
*3145		PCB No.52	< 4.6000 ng/l
*3148		PCB No.101	< 1.3000 ng/l
*3151		PCB No.118	< 1.1000 ng/l
*3154		PCB No.138	< 1.0000 ng/l
*3157		PCB No.153	< 1.5000 ng/l
*3160		PCB No.180	< 1.4000 ng/l
*3270		1 2 3-Trichloro-Benzene	7.0000 ng/l
*3271		1 2 4-Trichloro-Benzene	< 22.8000 ng/l
*3273		1 3 5-Trichloro-Benzene	< 10.6000 ng/l
*3276		Aldrin	< 0.4000 ng/l
*3294		DDE-(PP')	< 0.3000 ng/l
*3295		DDE-(OP')	< 0.5000 ng/l
*3296		DDT (OP')	< 2.5000 ng/l
*3297		DDT (PP')	< 0.3000 ng/l
*3301		Dieldrin	< 0.5000 ng/l
*3303		Endosulphan A	< 0.5000 ng/l
*3304		Endosulphan B	< 1.7000 ng/l
*3306		Endrin	< 0.9000 ng/l
*3310		HCH Alpha	0.4000 ng/l
*3311		HCH Beta	15.5000 ng/l
*3312		HCH Delta	< 0.8000 ng/l
*3313		HCH Gamma	0.8000 ng/l
*3329		TDE (OP')	< 1.5000 ng/l
*3330		TDE (PP')	< 0.5000 ng/l
*3335		Trifluralin	< 9.9000 ng/l
3375		Organochlorine pesticide preparation	1.0000 Misc
*3737		PCB No 31	< 1.5000 ng/l
*3738		PCB No 105	< 1.4000 ng/l
*3739		PCB No 156	< 1.7000 ng/l

'*' Indicates that Laboratory Determination Method is NAMAS Accredited.

APPENDIX 2

APPENDIX 3

The Environment Agency
National Laboratory Service
Exeter Laboratory, Manley House
Kestrel Way, Exeter EX2 7LQ
Tel: 01392 444000
Fax: 01392 442030 GTN 7-24- X

ENVIRONMENT AGENCY

memorandum

To Rob Hocking

From Rachel Brown

Extension number 2397

Date: 7th June 1996

RE: ANOMALOUS POSITIVE TBT RESULTS - RUN BIO5/19-MAR-96/069

I have investigated all the queried results and appropriate amendments have been made on Mensar. Because of these errors we now have a procedure in place that will immediately identify any false positives:

The problem was the result of interfering peaks on the chromatography, but can be compensated for by blank-correcting all the results. This is now a routine procedure for all organo-tins. As a further safeguard, we now check all positive organo-tin results by GC-MS, which will then be qualified as 'confirmed by GC-MS', 'not identified by GC-MS' (in which case an unusual MRV may have to be used) or 'not possible to confirm by GC-MS' - i.e. it was impossible to rerun the sample due to, for example, matrix effects, insufficient sample and so on. This will appear in the comments field on Mensar.

I hope that this will prevent any future errors, but please let me know of any problems.

R. BROWN
Scientist (Organics)